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Laser-Induced Electrodeposition of Polyaniline on a Gold Electrode

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Maskless local electrodeposition of polyaniline (PANi) on a gold electrode has been achieved by electropolymerization of aniline in a neutral electrolytic solution with an aid of laser irradiation. It was found that PANi can be deposited on the laser irradiated sites even at relatively lower anodic potential.

Electropolymerization of some monomers like pyrrole, thiophene, and aniline, is one of the convenient methods for preparing thin films of conductive polymer on an electrode surface.[1-3] Since conductive polymer is now directed to the applications in the fabrication of microelectronic devices,[4] an improved technique for the selective area deposition is required. In the previous works,[5-7] photoassisted deposition technique has been used for the preparation of polypyrrole or polythiophene on a semiconductor (such as n-TiO_2 or silicon) electrode. The characteristic feature of this process is that monomer can be polymerized from an electrolytic solution by the photogenerated holes in the valence band of a semiconductor. Consequently, the deposition occurs only at photo-irradiated sites without any mask fabrication. However, the area-selective direct deposition of conductive polymer on a smooth metallic electrode has not been reported yet.

In this communication, we report the results, for the first time, about the electropolymerization of aniline on a smooth gold electrode from a neutral electrolytic aqueous solution with an aid of laser irradiation. This method enables us to deposite PANi in the local region of laser irradiated sites at relatively lower anodic potential.

All chemicals used in this study were of reagent grade which were purchased from WAKO Chemical Co. Ltd. Aniline was purified by distillation. Solutions were prepared using Milli-Q water and were deoxygenated with nitrogen gas before use.

Experiments have been carried out in a single compartment photoelectrochemical(PEC) cell with the standard three electrode configuration. A gold working electrode(10mm × 10 mm, Nilaco), was finely polished with 1- and 0.05 μm alumina slurries before use. Electropolymerizations were performed in an aqueous solution containing 0.05 M aniline monomer and 0.1 M KCl electrolyte (pH=6.7). A Nd:YAG laser (1064 nm) was used as a light source to illuminate the electrode surface. The diameter of the laser beam on a gold electrode was ca. 200 μm. Deposited PANi on the electrode surface was characterized by FT-IR reflectance microspectroscopy (IMS-8000, Shimadzu).

Aniline has been generally polymerized electrochemically at the electrode potential more positive than +0.8 V vs. SCE in an aqueous solution.[8] However, the polymerization of aniline occured at +0.65 V vs. SCE when the surface of electrode was exposed to laser irradiation. The product deposited on the laser irradiated area was compared with that on the unirradiated regions using FT-IR reflectance microspectroscopy. The spectrum in Fig. 1(a) was obtained from the area without laser irradiation, whereas Fig. 1(b) was obtained from the the deposit formed on the laser irradiated site. No spectral features could be observed in Fig. 1(a), and this fact indicates that the film thickness on the surface is too thin to be detected (probably no film was formed on the surface). Figure 1(b) shows a distinct infrared spectrum of PANi. This means that the growth rate of PANi was significantly enhanced at the laser irradiated site. Absorption peaks at 1585 and 1502 cm^{-1} correspond to the C=C stretching vibrational mode of aromatic ring structure, and the peaks at 1308 and 1250 cm^{-1} correspond to the stretching of C-N bond of secondary aromatic amine.[9]

Since the infrared absorbance can be used to estimate the amount of PANi deposition, the dependence of film thickness of PANi on the electrolysis time was ex-situ studied with FT-IR microspectroscopy. Figure 2 shows the absorbance at 1308 cm^{-1} as a function of the electrolysis time with and without laser irradiation. The electrode potential was set at +0.7 V vs. SCE. It is quite clear that the absorbance was increased

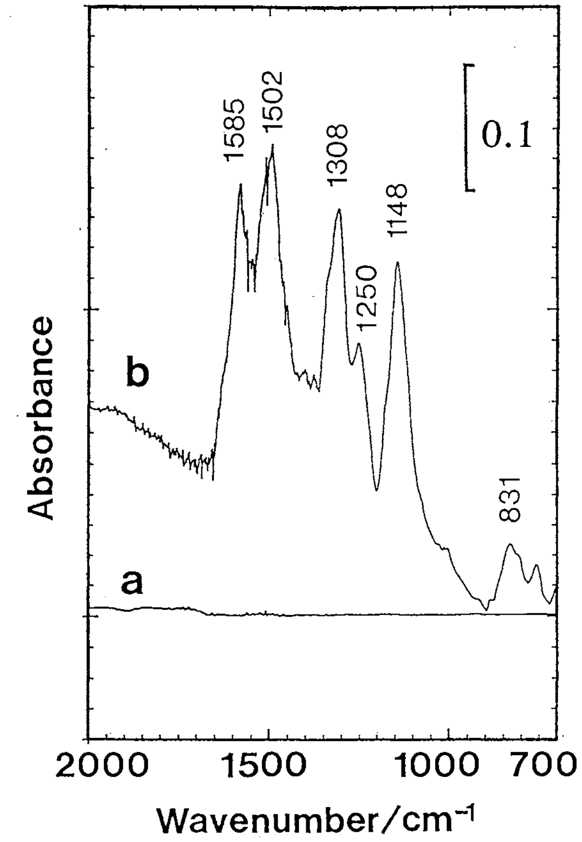

Fig. 1. Infrared spectra of deposit measured by FT-IR microspectroscopy. (a) Areas without laser irradiation and (b) areas with laser irradiation.

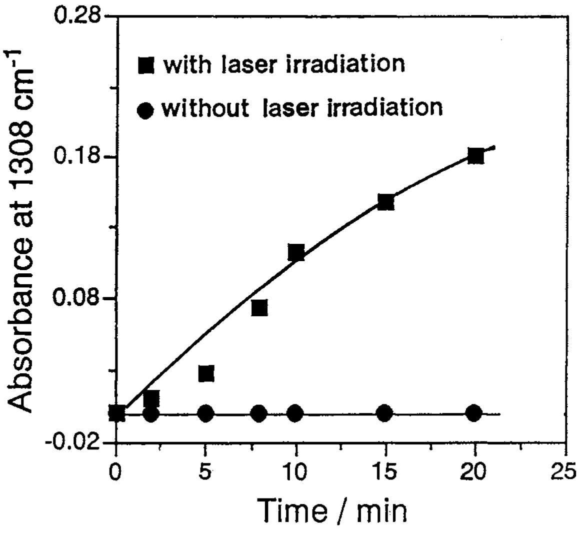

Fig. 2. Dependence of the absorbance at 1308 cm^{-1} on the electrolysis time. The electrode potential was set at +0.7 V vs. SCE. (■) with laser irradiation(300 mW), (●) without laser irradiation.

as the electrolysis time increased under the laser irradiation (Fig. 2, upper curve). On the other hand, no increase of absorbance was observed even when the electrolysis time was prolonged to 1 h(Fig. 2, lower curve). Accordingly, it is confirmed that the growth of PANi is induced by the laser irradiation. As for the electropolymerization of aniline in a electrolytic solution of pH>4, it is known that an electroinactive PANi film is formed.[10] This electroinactive film would inhibit the further formation of PANi film. Thus, in general, the deposition does not proceed further in case that the electrolysis is performed without laser irradiation. However, the electrodeposition in an electrolytic solution of pH=6.7 used in this study did proceed without any decrease of deposition rate under the laser irradiation, as is shown in Fig. 2.

Laser-induced elelctrodeposition on PANi was also strongly influenced by the electrode potential. We found that the deposition did not occur until the potential was applied at more positive than +0.65 V vs. SCE . The deposition rate at laser irradiated site was gradually increased with increasing the electrode potential. When the potential was applied at more positive than +0.9 V vs. SCE, a brown PANi film was also formed on the region unexposed to the laser light, as previously reported.[10,11] Therefore, it is suggested that the area selective PANi electrodeposition on a gold electrode takes place at the potential window between +0.65 to +0.9 V vs. SCE. Figure 3 shows a microphotograph of PANi formed at the focal point of laser beam on a gold electrode. This deposition was achieved after keeping the electrode at +0.7 V vs. SCE for 10 min under 300 mW laser irradiation. The spot size of the deposit was ca. 330 μm in diameter, and was almost unchanged with electrolysis time. When the electrode was scanned by manual movement of the microscope stage, a deposition pattern was produced along the scanning path. Accordingly, the laser-induced electrodeposition can be used for limited area processing and custom patterning in fabrication of microelectronics.

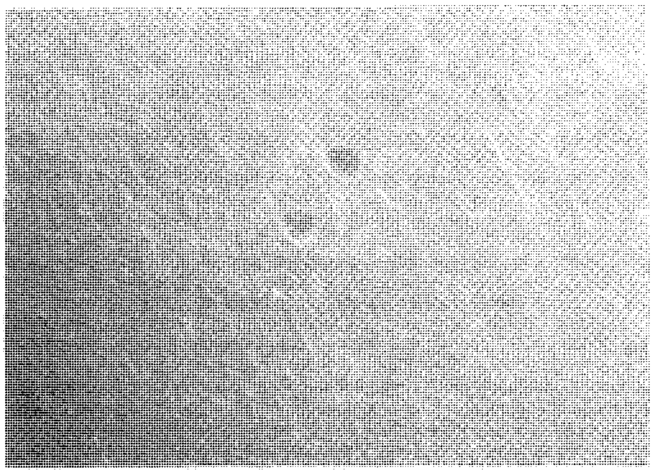

Fig. 3. Microphotograph of a deposit of PANi(330 μm in diameter) formed on a gold electrode.

In the case of semiconductor electrodes, the formation of a conductive polymer on a electrode surface with laser irradiation is ascribed to the photogenerated holes in the valence band.[5-7] This photolytic effect, however, seems hard to explain the characteristic features observed in our experiments. Paying attention to the fact that aniline monomer was polymerized at relatively lower potential, the laser-induced thermal effect is most likely to influence the kinetics of electrochemical process, because the temperature raising at the illuminated area on the electrode results in shifting the equilibrium potential.[12] Hence, the irradiated site, which is heated by laser, has a more positive potential than the potential applied on the non-irradiated part of the electrode.[13] Thus, the deposition occured at the irradiated site only. Further study is now in progress.

As a conclusion, the present study provided a new method for maskless, area selective deposition of conductive polymer(PANi) on a metal elelctrode surface. This result also leads to the deeper understanding of the fundamental factors(e.g. thermal or photolytic) influencing the electropolymerization of aniline.

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