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Conducting Pattern Formation of Electrochemically Polymerized Thiophene in an Organopolysilane Film Imaged by Ultra-Violet Light

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The electrochemical polymerization of thiophene was successfully performed in an organopolysilane film on an indium tin oxide (ITO) glass electrode as patterned by the Ultra-Violet (UV) light irradiation. It was demonstrated that only the UV-exposed polysilane dissolved into polar solvent such as propylene carbonate used as electrolytic solvent and hence electrochemical polymerization proceeded on the ITO electrode masked with the UV-unexposed polysilane. Fine line patterns of 10 μm width were obtained.

A great deal of interest has been paid on organopolysilanes consisting of Si backbone and two organic side groups on each Si atom as a new class of functional polymeric materials with unique physical and chemical properties due to significant delocalization of σ-electrons along the polymer chain, which is different from the conventional carbon-based polymers.[1)] The physical properties of organopolysilanes are especially characterized by their high hole drift mobility as much as 10^{-4} $cm^2V^{-1}S^{-1}$ [2-4)] and have been extensively investigated for their application as a charge carrier transporting polymeric material in electrophotographic photoreceptors.[5-8)] While the doping with an oxidizing agent such as SbF_5 or AsF_5 has been found to give semiconducting polymers, the doped organopolysilanes are unlikely useful practically because of their lability that they react rapidly with air and moisture. On the other hand, organopolysilanes are also characterized by the chemical nature that they easily undergo the photodecomposition to scissor Si-Si bond of the backbone and form Si-O-Si and Si-OH bonds by oxidation when exposed to ultra-violet (UV) light in air. In addition, the photodecomposition by UV light (300-400 nm) proceeds as patterned from surface to bulk of the film due to the so-called self-bleaching of the σ-σ* absorption band. This property of organopolysilanes has led to the possible application to lithography[9)] and has been suggested the possibility as memory devices.[8,10)] Furthermore, the hydrophilic Si-O-Si or Si-OH formation ascribable to the photodecomposition interestingly induces the wettability or swelling effect for water. From this point of view, our previous work successfully demonstrated that organopolysilane films patterned by UV light are selectively dyed only in the UV-exposed area with water soluble dyes.[11)]

In the present letter, for developing further utilization of the swelling effect, we have tried to polymerize thiophene electrochemically only in the UV-exposed area of organopolysilane films and succeeded in forming electroconducting fine patterns as imaged by UV light. The pattern polymerization of thiophene has been confirmed to proceed as a result of the difference in solvent dissolution properties between the UV-exposed and the UV-unexposed areas of the film.

Organopolysilane selected was phenylmethylpolysilane (PMPS), which was prepared by the Wultz-coupling of phenylmethyldichlorosilane monomers with sodium metal in toluene according to the literature.[12] The molecular weight (Mw) of PMPS was several 10^4 as measured by GPC using polystyrene for calibration. PMPS films of ~1 μm thickness were prepared on indium tin oxide (ITO) glass substrates by spin coating and dried at 60 °C. The films were exposed to the UV light (10 mW/cm^2 at 310 - 400 nm) from a Hg lamp (TOSCURE 401, Toshiba) through a pattern photomask, usually for 5 min, and then were set as a working electrode in an electrolytic solution containing 0.1 M thiophene, 0.05 M 2,2'-bithiophene, or 0.033 M 2,2':5',2"-terthiophene as a thiophene monomer and 0.1 M tetraethylammonium tetrafluoroborate as a supporting electrolyte in propylene carbonate (PC). Electrolytic polymerization was carried out by applying a constant voltage vs. saturated calomel electrode (SCE) as a reference electrode with potentiostat (HA-301, Hokuto Denko Ltd.) under a nitrogen atmosphere.

When thiophene was used as a monomer, the relatively high voltage (> +2.1 V vs. SCE) required for the polymerization caused the deterioration of PMPS films, and hence led to uneven pattern formation. Such deterioration may be attributed to the oxidation of the UV-unexposed polysilane film near film edge or pin holes. While, in the case of using 2,2'-bithiophene or 2,2':5',2"-terthiophene, the pattern polymerized films were easily obtained at relatively lower voltages of +1.1 or +0.9 V vs. SCE, respectively. Figure 1 shows a typical polythiophene (PT) pattern obtained for 2,2'-bithiophene as imaged by the UV light pre-irradiation through a micro-patterned photomask. In the figure are illustrated the micro-patterns of 90 x 90 μm using a color filer pattern for TFT(Thin Film Transistor)-driven liquid crystal display.

At the initial stage, we started this work from the viewpoint of the utilization of swelling effect of UV-exposed polysilane films. In general, however, it is known through lithographic studies concerned that UV-exposed polysilanes are dissolved into polar solvents such as alcohols.[9] Since PC used here was one of the

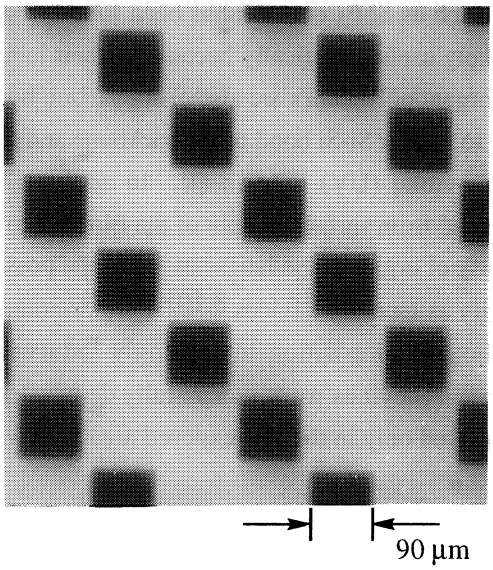

Fig. 1. PT pattern obtained for 2,2'-bithiophene as imaged by the UV light pre-irradiation. The square pattern in the photograph indicates the dark blue PT.

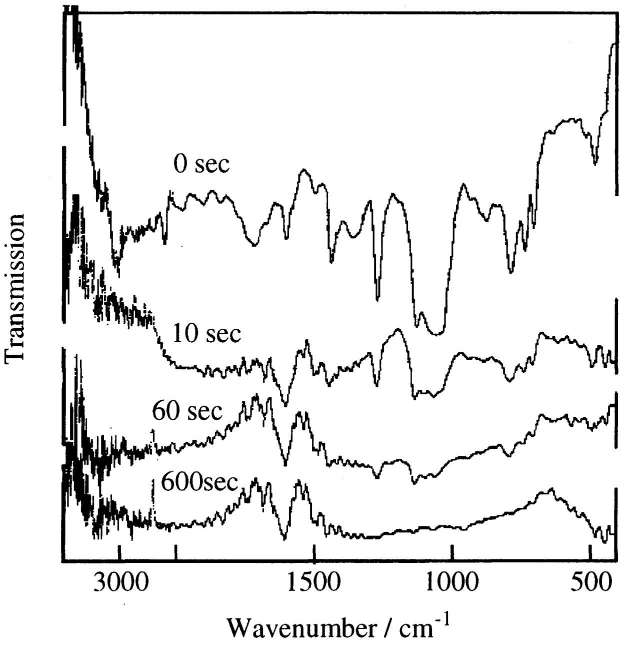

Fig. 2. FT-IR spectra of UV-exposed films as a function of immersion time in PC.

polar solvents, the dissolution of UV-exposed films was examined by FT-IR spectroscopy and SEM measurements for the samples immersed into PC and then dried. Figure 2 shows the FT-IR spectra of UV-exposed films as a function of immersion time in PC. The characteristic band to be attributable to Si-O-Si near 1100 cm^{-1} was found to disappear completely after immersion for only 10 min. The dissolution of UV-exposed polysilane into PC was more clearly confirmed in the SEM image, in which the only UV-exposed area was disappeared. In order to clarify the solubility difference between UV-exposed and unexposed PMPS films, similar dissolution tests were made for a variety of solvents by means of FT-IR and electron spectroscopy for chemical analysis (ESCA) to determine the existence of polysilanes left on the substrate. The results are listed in Table 1, being classified with E_T^N values as empirical parameter of solvent polarity.[13)] In solvents with the E_T^N value > about 0.355, UV-unexposed PMPS is insoluble. However, UV-exposed PMPS becomes soluble in the solvents with the E_T^N value < about 0.790, that is, more soluble because of the formation of much polar Si-O-Si and/or Si-OH bonds and the lowering of molecular weight by the UV light irradiation. The solvent, PC, with the E_T^N value of 0.491 was most favorable to make the difference in solubility between UV-exposed and unexposed polysilanes, which enabled the electrochemical polymerization of thiophene on the bared ITO glass substrate as patterned by the UV light irradiation.

Table 1. Dependence of solubility of UV-exposed and unexposed PMPS films on E_T^N values as empirical parameter of solvent polarity[13)]

Solvent	E_T^N	PMPS films	UV-exposed PMPS films
Water	1.000	Insoluble	Insoluble
Formamide	0.799		
1,2-Ethanediol	0.790		
Methanol	0.762		Soluble
N-Methylacetamide	0.657		
Ethanol	0.654		
Acetic acid	0.648		
1-Butanol	0.602		
2-Propanol	0.546		
Propylene carbonate	0.491		
Acetonitrile	0.460		
Acetone	0.355		
1,2-Dichloroethane	0.327	Soluble	
Nitrobenzene	0.324	Almost soluble	
Chloroform	0.259	Soluble	
Cyclohexane	0.006	Soluble	

In Fig. 3 is shown a SEM image of thiophene polymerized electrochemically for 3 min at 1.2 V vs. SCE. From the figure, the fine PT lines of about 10 μm width (thickness : about 0.5 μm) were clearly shown to form only in the UV-exposed area, i.e., only on the bared ITO substrate. Thus, it has been demonstrated that the only UV-exposed area of the PMPS films were dissolved into the electrolytic solution and electrochemical polymerization of thiophene proceeded on the ITO electrode covered with the unexposed PMPS. Moreover, it would be anticipated to obtain patterned films of PT by choosing an appropriate solvent such as N,N-dimethylformamide, acetonitrile, or sulfolane with the E_T^N value between 0.355 and 0.762 from Table 1.

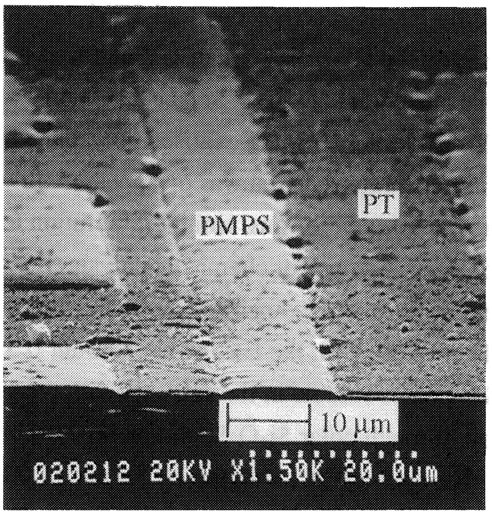

Fig. 3. SEM image of thiophene polymerized electrochemically only in the UV-exposed PMPS area on the ITO electrode.

Conductivity of the PT pattern stripped from the electrode was measured by a four-probe technique at room temperature. The result indicated that PT obtained has the conductivity of several S/cm in agreement with that measured for PT heretofore.[14)]

More interestingly, the PT patterned films exhibited electrochromic behaviour due to redox equilibrium as is observed in the usual PT films. The red colored pattern of undoped state at the voltage of 0 V vs. SCE clearly changed into blue as patterned at 1.2 V (doped state), with spectral change around 470 nm peak. From the cyclic voltammetry measured by applying the continuous triangular wave voltages between 0 and 1.2 V, the lifetime of PT was satisfactory and the PMPS film was stable even after 1000 cycles. These facts enable us the fabrication of the display device without etching ITO substrates for desired patterns.

In conclusion, we have succeeded in polymerizing thiophene electrochemically as patterned only in the UV-exposed polysilane film utilizing the photodecomposition of organopolysilanes as well as in forming electroconductive fine lines. The difference in dissolution properties for solvents between UV-exposed and unexposed PMPS was found to give the formation of the pattern PT. The method described here seems to indicate the potential application to a display device without etching the ITO substrate for pattern.

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