Pattern Coloring of UV-Light Imaged Polysilane Films Using Electrochemical Deposition of Pigment Micelle

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The patterned deposition of pigments in a UV-light imaged polysilane film coated on an indium tin oxide glass electrode was successfully performed utilizing photo-induced swelling effect of polysilane and the electrochemical deposition technique of pigment micelles. The result enables us to fabricate the multicolor patterns on the same film with successive electrochemical depositions of different colored pigment micelles, simply repeating the procedures of UV-pattern exposure, electrochemical pigment deposition, washing with water, and drying.

A great deal of interest has been paid on organopolysilanes (polysilanes) 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 are different from the conventional carbon-based polymers.[1] The physical properties are especially characterized by their high hole drift mobility as high as 10^{-4} cm^{2}V^{-1}s^{-1},[2-4] and have been extensively investigated for their application as a charge carrier transporting material in electrophotographic photoreceptors.[5-8] The σ-conjugation in the Si backbone has also prompted to explore the possible utilization as a film material for the third-order non-linear optics.[9,10] On the other hand, it is well known as their chemical properties that polysilanes exposed to ultra-violet (UV) light easily undergo the photodecomposition, which forms Si-O-Si and Si-OH bonds as a result of Si-Si bond scission of the backbone, especially 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 spectral self-bleaching of the σ–σ* absorption band. This property has led to the possible application to lithography [8] and the possibility as memory devices has been suggested.[9,10] Furthermore, it can readily be imagined that the formation of Si-O-Si or Si-OH only in the UV-exposed area of the film causes various changes in physical and chemical properties from those of the unexposed area, e.g., in the mechanical properties due to incorporation of much flexible Si-O-Si bonds, in the wettability or swelling for water due to the formation of hydrophilic group, and in the refractive index due to the shortening of σ-conjugation length in the Si backbone by incorporating different O atom and so on. From this point of view, we showed that polysilane films patterned by UV light were selectively dyed only in the UV-exposed area with water soluble dyes.[11]

In this letter, we have concentrated on the further application of swelling effect induced by UV irradiation among those and tried to make the coloring patterns with more durable pigments instead of water soluble dyes on the UV-imaged polysilane films by combining the micelle electrochemical deposition technique.[12]

As a typical polysilane, poly(methylphenysilane) (PMPS) was used, which was prepared by Wultz-coupling of methylphenyldichlorosilane monomers with sodium metal in toluene according to the literature.[13] The molecular weight (M_w) 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 electrolytic solution. The solution of pigment micelles was prepared in the following manner. An aqueous solution containing 2.0 mM Polyoxyethlene(13) 11-Ferrocenylundecyl ether (FPEG) surfactant, 0.1 M LiBr and 10 mM pigment was sonicated for 10 min and stirred for 3 days. Pigments used here were copper and titanyl phthalocyanines (CuPc and TiOPc, blue), chlorinated CuPc (CuPcCl$_{14}$, green) and anthraquinone pigment (AnQ, red). This solution was allowed to stand for more than 1h. The supernatant of this solution was used for electrochemical deposition. The micelle electrochemical deposition was carried out by applying a constant voltage vs. saturated calomel electrode (SCE) as a reference electrode with potentiostat (HA-301, Hokuto Denko Ltd.).

Figure 1 shows the cyclic voltammogram for electrochemical deposition at the UV-irradiated PMPS coated on ITO electrode in the 10 wt% acetonitrile aqueous solution containing 10 mM CuPc, 2.0 mM FPEG, and 0.1 mM LiBr. The anodic peaks at about 0.28 V and 0.68 V vs. SCE could be assigned to the oxidation of FPEG [12] and CuPc [14], respectively. Interestingly, deep blue coloration occurred beyond 0.7 V vs. SCE. This means that CuPc pigment particles accumulated in the polymer film should become sufficiently conductive for the successive oxidation of FPEG at

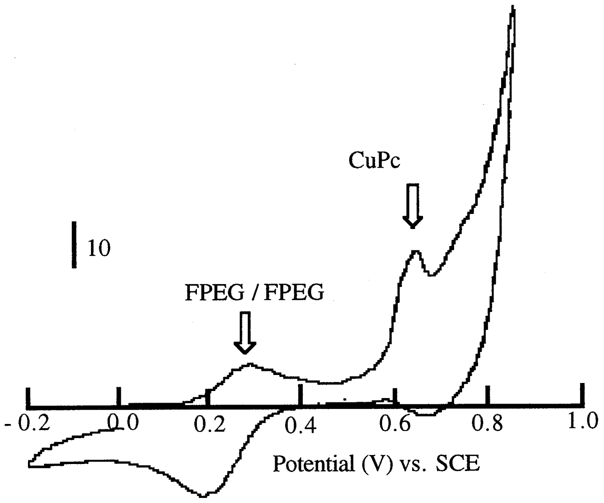


Figure 1. Cyclic voltammogram for a 10 wt% acetonitrile aqueous solution containing 10 mM CuPc, 2.0 mM FPEG, and 0.1 mM LiBr. Scan rate is 10 mV·sec^{-1}. Working electrode is ITO electrode covered by the UV-irradiated PMPS.

the most front interface of piled pigments in the polymer, although the oxidation of FPEG at 0.28 V leads to the destruction of pigment micelle.[12] The blue coloring of the UV-irradiated PMPS was then carried out by controlled potential electrolysis at higher than +0.7 V vs. SCE while slowly stirring the solution.

Figure 2 shows a typical coloring pattern obtained for CuPc micelles 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.

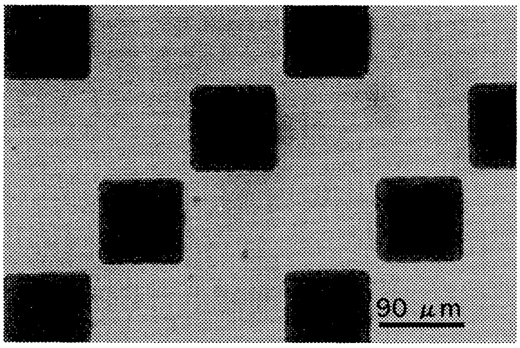
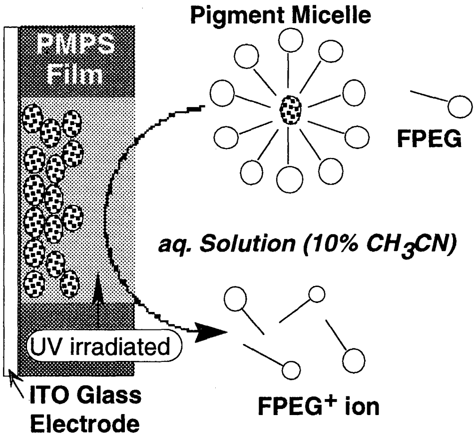


Figure 2. Typical coloring pattern obtained for CuPc micelles as imaged by the UV light pre-irradiation through a micro-patterned photomask. The dark square pattern indicates the blue colored micelle electrochemical deposition pattern in the photograph.

In the FT-IR spectra of UV-exposed films before and after coloring with TiOPc, the characteristic band attributed to Si-O-Si near 1100 cm^{-1} was found even after coloring by micelle electrochemical deposition. Therefore, the dissolution of UV-exposed polysilane into aqueous solution seemed hardly to take place. Consequently, the present coloration of polysilane film would be considered as illustrated in scheme 1. The pigment micelles diffusing into the UV-irradiated polysilane which was swollen by aqueous solution, was broken in the film over the oxidation potential of FPEG (+0.3 V vs. SCE) to leave the water-insoluble pigment particles only in the UV-irradiated portion of PMPS films. Actually, the size of pigment micelles was crucial and the size used here was found to be about 140 nm as measured with the dynamic light scattering method. To promote the successive oxidation of FPEG effectively at the front surface of the pigments piled up, the potential over oxidation of pigments to be conductive would be required as discussed above.

More interestingly, the colored portion by electrochemical deposition looses the swelling to water no longer when dried at higher than 60 °C. This result suggests that multicoloring pattern with different colored pigments is possible on the same polymer film by repeating the coloring procedures with displacing UV-imaged area successively.

In conclusion, we have successfully demonstrated the pattern coloring of polysilane films with pigments combining the swelling effect induced by their unique UV-photodecomposition with the micelle electrochemical deposition technique. The well-resolved micro-pattern was found to be reproducible. Since, moreover, it was found possible to fabricate the multicolor patterns in the same film with successive electrochemical depositions of different colored pigments, simply repeating the procedures of UV-pattern exposure, electrochemical pigment deposition, washing with water, and dying, the present processes developed would be applicable to micro-patterned color filter fabrications in TFT-driven liquid crystal display as a new technique.



Scheme 1. A plausible mechanism for the present coloration of polysilane film.

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