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Ultra-Violet Photodecomposition of Polysilanes and its Novel Application to Xeroprinting System

Masaaki Yokoyama, Yuji Hiroshige, Yasuhiro Yamaguchi,
and Mikio Kakui

Chemical Process Engineering, Faculty of Engineering,
Osaka University,
Yamadaoka, Suita, Osaka 565

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As a unique application of organopolysilanes, a novel xeroprinting system has been developed in a simple configuration comprising only a hole-transporting layer of organopolysilane coated on a hole-injecting metal substrate. A persistently stored image due to photodecomposition, formed by the ultra-violet (UV) exposure through a photo-mask to the organopolysilane, can be read out repeatedly as many copies by simply charging the free surface negatively and developing with toner. The printing process using a UV-imaged master can be performed under room-light. This system will be promising in a growing field of small-volume printing replacing the conventional wet offset printing.

KEYWORD: organopolysilane, UV-photodecomposition, formation of insulator, xeroprinting master, multiduplication

§1. Introduction

Organopolysilanes having a σ-conjugated Si backbone have recently attracted considerable attention as a new class of functional materials in view of their unique physical and chemical properties different from conventional carbon-based polymers. Particularly, the extraordinarily high hole mobility, of the order of 10^{-4} cm^2/Vs, for amorphous polymeric materials has stimulated many investigations on their application to photoreceptors for xerography. Double-layered photoreceptors composed of an organopolysilane-based charge transport layer (CTL) and a charge photogenerating layer (CGL) (e.g., amorphous selenium[1]); phthalocyanine-dispersed polymer[2,3]) have already been found to exhibit high xerographic sensitivity. On the other hand, organopolysilanes possess a unique photochemical characteristic as well: when exposed to ultra-violet (UV) light in the presence of oxygen, they undergo the Si-Si bond scission of the backbone chain, which is characteristically accompanied by the Si-O-Si bond formation. Although the photodecomposition itself in polysilanes has been well investigated from the viewpoint of practical application as a photoresist in lithography, the Si-O-Si bond formation is expected to cause various changes in physical properties of polysilanes, e.g., deterioration of the charge-transporting ability as well as an increase of the ionization potential due to the shortening of σ-conjugation in the Si backbone.

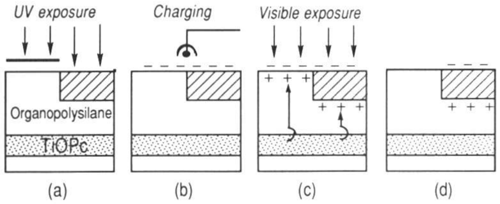

Fig. 1 Electrophotographic duplication using organopolysilane-based memory photoreceptor. (a) structure of layered photoreceptor and per sistent image formation due to the UV photodecomposition, (b) corona charging, (c) xerographic image readout by uniform visible light exposure, and (d) electrostatic latent image on the UV imaged region.

In our previous papers,4,5) we successfully developed a new type of memory xerographic photoreceptor positively utilizing such a unique property of photodecomposition as shown in Fig.1. The memory photoreceptors have a conventional CTL-CGL configuration. The imagewise UV exposure to the CTL of organopolysilanes affords the persistent image storage as the result of the above-mentioned photochemical reaction, i.e., the formation of an insulator with no hole transporting ability. The reading-out of the stored image can be performed by the usual xerographic method, i.e., by uniform visible light irradiation following negative charging to photogenerate charge carriers. In the UV unexposed areas, the negative surface charges are neutralized by the positive charges (holes) photoinjected from the CGL through the CTL when irradiated by the visible light, while in the UV exposed areas, the photoinjected holes are effectively blocked at the photodecomposed polysilane layer to leave a residual potential depending on the thickness of the photodecomposed blocking layer. Then, the residual potential can be visualized by the usual toner development. We reported that this memory photoreceptor is promising for an electrophotographic multiduplication system. Unfortunately, however, this system unavoidably requires uniform visible light irradiation for charge generation in every printing process.

In the present paper, we would like to introduce our recent work that we have succeeded in solving the problem by using, in place of the CGL, such a metal electrode that can inject holes into the CTL even in the dark. This paper describes the working mechanism and has demonstrated the potential of the practical use as a new type of xeroprinting system.

§2. Experimental

As a typical organopolysilane, poly(methylphenylsilylene) (PMPS), which surpasses others in film-forming ability, was used in this work. PMPS was prepared by the Wurtz coupling of methylphenyldichlorosilane (Shin-etsu Chemicals Co., Ltd.) with sodium in toluene according to the literature.5) The polymer obtained was purified by repeated precipitations from toluene with ethanol, and the molecular weight Mw was 1.2 x 10^4 as measured by gel permeation chromatography using polystyrene standards. As hole injection electrodes (HIEs), Pt, Cu, and Al were evaluated. The Pt electrode (thickness: ca. 0.1 μm) was prepared on aluminum sheets or ITO coated polyester films by ion sputtering (E-102, Hitachi Nakaseiki Co., Ltd.), and commercially available foils of Cu and Al were used. Amorphous films of PMPS were cast from tetrahydrofuran solution onto these electrodes (for charge acceptance measurements) and a quartz glass (for electronic absorption measurements) by a wired-bar or spin-coating technique and then dried in air at 80 °C for 30 min. The films were exposed to 340-nm light (2.5 mW/cm^2) from a xenon lamp through an interference filter (KL-34, Toshiba Glass Co., Ltd.). Dark decay of the surface potential was measured with an electrostatic paper analyzer (EPA-8100, Kawaguchi Electric Works Co., Ltd.) The samples set on a turning table were charged negatively by passing them under a 7.5-kV corona wire with a rate of 5 m/min. The surface potentials from 0.5 s later after charging were measured as a function of time.

The photoelectron emission from the PMPS and HIEs used in this work was measured as a function of incident photon energy with a photoelectron emission analyzer (AC-1, Riken-keiki Co., Ltd.). The threshold energy for the emission gives the work function for the metals and the ionization potential, IP, for insulators. No photoelectron emission from the UV decomposed PMPS was observed in the energy range available in the analyzer (3.5 - 6.2 eV), indicating that the IP of the decomposed PMPS should be located beyond this range (i.e., IP > 6.2 eV).

§3. Results and Discussion

3.1 *Concept of Multi-duplication Xeroprinting System*

Figure 2 shows the principle of the multi-duplication xeroprinting system developed in this work. The device consists simply of a PMPS layer on a hole injecting metal electrode (HIE).

The imagewise UV-irradiation through a photomask produces the photodecomposed insulating polysilane layer, which acts as a blocking layer for the hole transport. Fortunately, UV photodecomposition of organopolysilanes proceeds as patterned, from the surface to the bulk depending on the UV exposure because of the so-called self-breaching based on spectral shift to the shorter wavelength in photodecomposed polymer. During corona charging, the injected holes leave the electrostatic latent image only on the insulating layer which was UV-imaged. The surface potential on this insulating layer is proportional to the thickness of the photodecomposed layer. Toner development, followed by toner transfer on plain paper produces a negative image printing. The repetition of the processes (b) and (c) affords us the multi-duplication without *every* image exposure. The key point for developing this process is, therefore, to explore the metal electrode from which the holes are effectively injected into PMPS even *in the dark*.

3.2 *Hole Injection into PMPS from Metals*

Stolka et al. reported that the contacts between PMPS and carbon gold or graphite are near ohmic.[1] We examined the negative-charge acceptance of PMPS (IP=5.62 eV) on metals of different work functions; Al (ϕ_{obs}=4.13 eV), Cu (4.56 eV), and Pt (5.34). As shown in Fig. 3, the charge acceptance decreased with an increase in the work function. This observation suggests that holes are injected into the PMPS from these metals by Schottky emission. It should be noticed here that PMPS in contact with Pt can accept little negative charge. This result is consistent with only a little energy barrier (0.2 eV) for hole injection between PMPS and Pt.

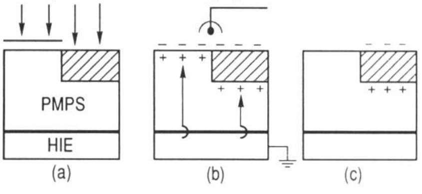

Fig. 2 The principle of the xeroprinting system: (a) persistent image storage due to UV photodecomposition (the hatched part represents the photodecomposed insulator layer), (b) the electrostatic image formation by negative charging, and (c) electrostatic image on the receptor.

3.3 *UV Photodecomposition of PMPS*

PMPS exhibits a strong σ-σ* absorption band ($\lambda_{max.}$ = 340 nm) as shown in Fig. 4. From the decrease in the absorption based on the UV exposure (340 nm), the energy flux required to photodecompose a 1-μm-thick layer of PMPS was determined to be 3.53 J/cm^2. The photodecomposition results in the shortening of the σ-conjugation because of the insertion of oxygen atom in its backbone chain, which could deteriorate the hole-transporting ability since hole transport in organopolysilanes has been reported to be a hopping process with σ-conjugated domains as hopping sites.6,7)

Figure 5 shows the hole mobility in the copolymers prepared from dichloromethylphenylsilane and 1,3-dichloro-1,3-dimethyl-1,3-diphenyl disiloxane as monomers. The increasing contents of oxygen atoms give rise to decreasing

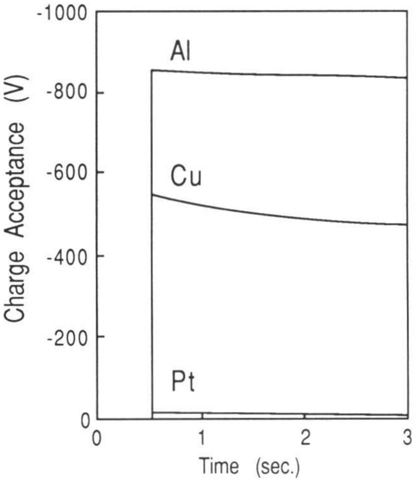

Fig. 3 Surface potentials of PMPS (10 μm thick) on various metal substrates as a function of time after charging.

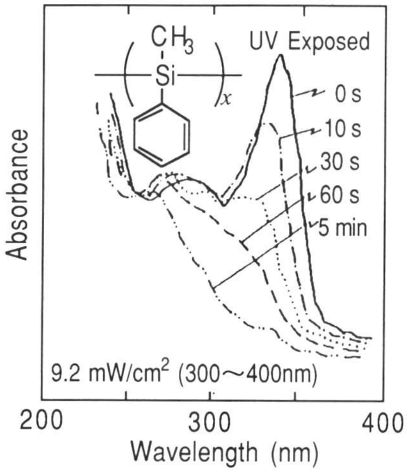

Fig. 4 UV spectra of PMPS films and their spectral change upon the UV exposure.

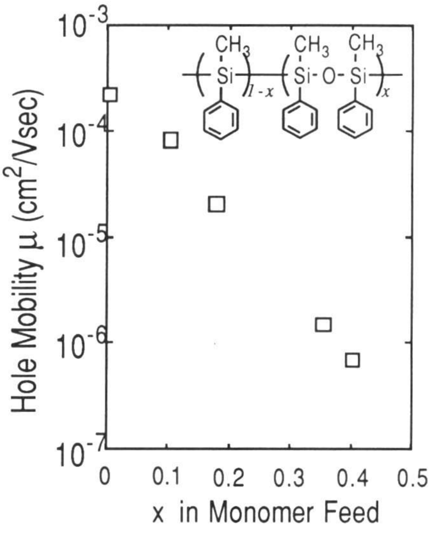

Fig. 5 Hole mobility in the copolymers containing oxygen atoms in their Si backbone chain.

hole mobility. Our previous work indicated that the photoinjected holes into the PMPS from a CGL are effectively blocked at the UV photodecomposed layer.[3,4] We believe that this blocking is due to the deterioration of hole-transporting ability in the decomposed layer and/or due to the large energy barrier between the undecomposed (IP=5.62 eV) and decomposed (IP > 6.2 eV) layers.

Figure 6 shows the variation of the charge acceptance of a 5-μm PMPS film on Pt as a function of the UV pre-exposure energy. As expected, the charge acceptance increased proportionally with an increase in the UV exposure, i.e., with the penetration depth of UV decomposition. This behavior is favorable for gray-scale image reproduction. The intersection between the increasing and level regions gives 17.5 J/cm2, which is in good agreement with the exposure energy (17.65 J/cm2) required to photodecompose the entire 5-μm PMPS film. These results indicate that the charge acceptance in the present system is determined by the hole injection from Pt into PMPS and that the injected holes are blocked effectively at the UV decomposed layer as illustrated in Fig. 2. From the data shown in Fig. 6, we can expect that the present system is a favorable candidate for xeroprinting, i.e., an electrostatic printing process designed to make multiple copies of a document with a master. Although various kinds of systems for this purpose have been proposed so far, our one is, in principle, characterized by high resolution, gray-scale reproduction, and simplicity of the master fabrication.

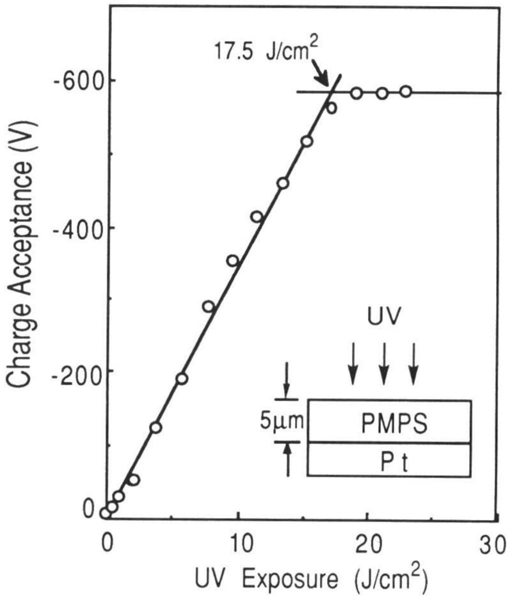

Fig. 6 Variation in charge acceptance due to the UV exposure (340 nm, 2.5 mW/cm2) for a PMPS/Pt receptor. The thickness of the virgin PMPS layer was 5 μm.

3.4 *Xeroprinting Using a UV-maged PMPS/Pt Master*

The printing test was carried out by sticking a present UV-imaged xeroprinting master with adhesive tape onto an aluminum drum of a commercially available laser beam printer (LP-X1, Mita Industrial Co., Ltd.). Simply by repeating the cycle of corona charging, toner development, and image transfer to paper with no light, i.e., without laser irradiation, fine negative printings (Fig. 7) of the photomask were obtained until the master was peeled off by the cleaning blade. Positive image printings are also obtainable by reverse development with an appropriate bias. At the present stage, no optimization in the geometrical configuration properties such as film thickness and gap-allowance of developing process have been carried out, but the printing image seems to be sufficiently capable of practical utilization.

3.5 *Shortening of Persistent Image formation*

Although the linear dependence of the charge acceptance on the decomposed layer thickness is favorable for the gray-scale image reproduction, the high charge acceptance is obtained only when the whole layer was photodecomposed, and the much higher energy flux of 17.5 J/cm2 was required for the 5 μm thick PMPS film. For practical use, the energy should be reduced for the persistent image formation due to UV photodecomposition. The search for sensitization processes in UV photodecomposition of organopolysilanes will be one avenue for shortening the memory formation time, but in the present work an alternative approach was made for this problem.

We adopted the UV irradiation through a transparent HIE, which produces the hole blocking layer from the rear-side adjoining HIE. For this purpose the Pt electrode was replaced with a transparent ITO glass or ITO coated polyester film. Figure 8 shows the variation of charge acceptance in a 6-μm thick PMPS film on an ITO glass as a function of the UV exposure. As shown in the data of absorbance (340 nm), about 19.5 J/cm2 was required to decompose the entire PMPS layer, while the charge acceptance leveled off at a high potential with much smaller energy of only 2.5 J/cm2. This result suggests that the photodecomposed PMPS layer of only about 1-μm thickness impedes completely the hole injection from ITO. The ITO substrate, however, gave the higher initial surface potential of 200 V similar to a Cu metal electrode (ϕ_{obs}=4.57 eV).

In order to reduce initial surface potentials in the PMPS/ITO receptors, the ITO surface was modified with a very thin layer of Pt to the extent of still being transparent, by ion sputtering. As shown in Fig. 9, the charge acceptance of the UV unexposed PMPS films on an ITO substrate decreased effectively with Pt deposition to give

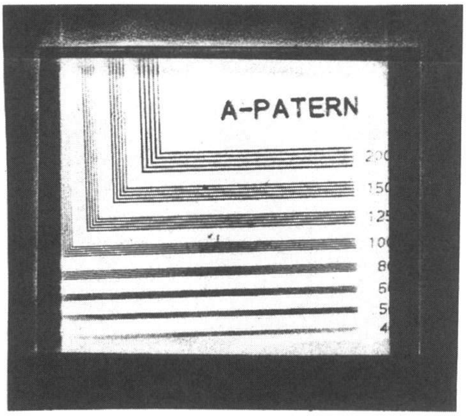

Fig. 7 A printing toner image.

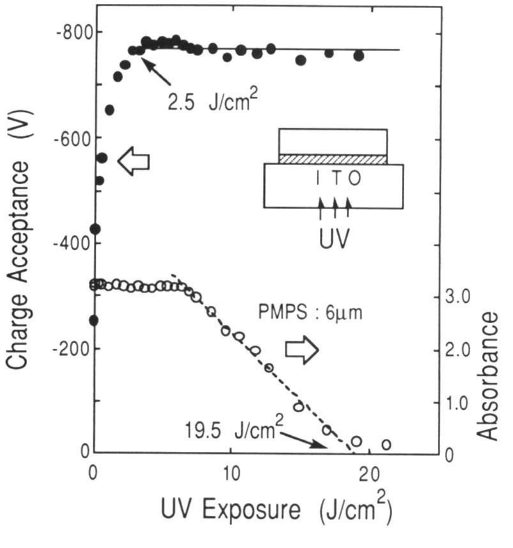

Fig. 8 The variation in charge acceptance due to the blocking layer formation for the hole injection by UV irradiation from rear-side through the ITO and absorption change in 340 nm of PMPS film.

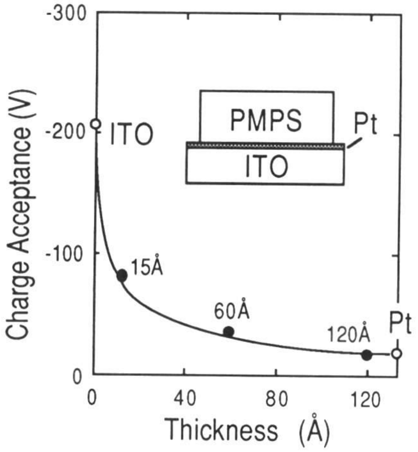

Fig. 9 Dependence of the charge acceptance in PMPS/ITO receptors on Pt deposition. Potentials were measured in a static mode with -6.5 kV DC corotorn.

the almost same potentials as the case of Pt metal. These receptors were also confirmed to give the fine printing images in the printing test. Judging from the favorable results and a very simple configuration, we conclude that this system is promising in a growing field of small-volume printing and may replace the conventional wet offset printing.

§4. Conclusion

We have developed a new type of xeroprinting system, which is based on the UV photodecomposition characteristic of organopolysilanes and effective hole injection from metals with a large work function. The present work has demonstrated one of the potential applications of organopolysilanes when the unique chemical and physical properties are successfully combined.

1) M. Stolka, H.-J. Yuh, K. McGrane and D. M. Pai, J. Polym. Sci. Polym. Chem. Ed. **25** (1987) 823.
2) K. Yokoyama and M. Yokoyama, Chem. Lett. **1989** (1989) 1005; K. Yokoyama, S. Notsu and M. Yokoyama, Denshi Shashin Gakkaishi, **29** (1990) 138.
3) T. Enokida, R. Hirohashi and R. Kurata, Nippon Kagakukaishi, **1990** (1990) 1005.
4) K. Yokoyama and M. Yokoyama, Appl. Phys. Lett. **55**, (1989) 2141.
5) K. Yokoyama and M. Yokoyama, J. Imaging Technol. **16** (1990) 219.
6) R. West, J. Organomet. Chem. **300** (1986) 327.
7) M.A. Abkowitz, M. J. Rice and M. Stolka, Philos. Mag. B. **61** (1990) 25.
8) K. Yokoyama and M. Yokoyama, Philos. Mag. B, **61** (1990) 59.