

Heat-Resistant Properties of a SiO₂-Coated PET Film Prepared by Irradiating a Polysilazane-Coated Film with Excimer Light

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Abstract

Flexible electronics have been recently paid much attention. A flexible substrate (Organic resin film) is indispensable component for flexible devices. Though PET film is low-cost organic film, low heat-resistance of PET film limits its application as a flexible device substrate. We have developed heat-resistant PET which does not deteriorate even at 190°C heat treatment for one hour. An excimer light was irradiated onto a polysilazane (PHPS: perhydropolysilane)-coated film to form a dense silicon-dioxide (SiO₂) layer on a PET film, and the heat-resistance property of the formed film was examined. Changes of surface state and cross-sectional structure of the formed film due to heat treatment were investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). Compared to normal PET, which is deteriorated and whitened by heat treatment of about 110°C - 120°C, the SiO₂-coated PET film maintains transparency and does not deteriorate after heat treatment at 180°C - 190°C for one hour. This high heat resistance is due to a dense SiO₂ film formed on the surface that prevents surface precipitation and crystallization of low-molecular-weight oligomers (which are the cause of thermal degradation of PET). It is expected that enhancing the heat resistance of PET—which has high versatility and low cost—to about 180°C to 190°C will allow SiO₂-film-coated PET to be developed as a film substrate for flexible devices.

Keywords

Polysilazane, Dense Silica Thin Film, Photo-Irradiation, Excimer Light, Heat Resistance, PET Film, Flexible Electronics

1. Introduction

In recent years, flexible electronics, which make it possible to produce flexible

devices such as flexible displays, electronics paper and solar cells, have been attracting attention [1]-[6]. A flexible substrate is an indispensable component for producing a flexible device, and an organic polymer film is usually used for that substrate. When various devices are fabricated on an organic polymer film, heat treatment—for processes like forming films on elemental devices and curing the film—is required. For that reason, the organic polymer film must have sufficient heat resistance. Accordingly, organic films with relatively good heat-resistance properties, such as polyimide (PI), polyethylene naphthalate (PEN), and polyether sulfone (PES), are used [7]-[11]. Known as “functional organic polymer films”, these organic films have the drawback that their cost is high. And the cost of the film is reflected in the final product. Although it may be possible to use PET as a general-purpose, low-cost organic film, the low heat resistance of PET limits its application as a flexible device substrate. For that reason, practical flexible devices using a PET film are few and far between.

We have developed a technology for forming a dense silica film at low temperature by irradiating a polysilazane-coated film with ultraviolet or excimer light. By utilizing the technology, we have succeeded in improving the gas-barrier properties of the organic polymer film [12] [13] [14]. It is expected that forming a dense silica film in this way will prevent surface deposition of low-molecular weight oligomers, which cause thermal deterioration of the PET film, and thereby improve the heat resistance of PET. PET films are known to contain cyclic oligomers with low molecular weight as natural impurities that are by-products generated during polymerization. Cyclic oligomers are precipitated on the PET surface after heat treatment, resulting in degradation of the PET such as reducing of transparency and flexibility [15] [16]. In the present study, the silica thin film was formed by irradiating an excimer light onto a polysilazane (PHPS: perhydropolysilane)-coated film formed on PET, and the heat-resistance characteristics of the formed PHPS-coated PET film were investigated and compared with those of a normal PET film. According to the results of the investigation, thermal degradation of normal PET starts around 110°C - 120°C, whereas the PET developed in this study has higher heat resistance—with almost no deterioration—even after heat treatment at 180°C - 190°C.

2. Experimental

2.1. Preparation of PHPS Film on PET Film and Formation of Dense SiO₂ Film by Excimer-Light Irradiation

A 5-wt% dibutyl-ether solution (ANL 120A, Sanwa Chemical Co., Ltd.) containing PHPS was spin-coated at 2000 rpm for 60 s onto a PET film (10 cm × 10 cm × 100-μm thickness, Toyobo Co., Ltd.), which has been subjected to hydrophilization treatment by ultraviolet (UV) irradiation. The prepared film was irradiated at 100°C for 2 min. with excimer light (irradiation intensity: 42 mW/cm²; MD COM., Ltd.). The thin film was formed on both sides of the PET film.

2.2. Evaluation of Heat Resistance

The prepared thin film was heat treated at temperatures of 90°C, 120°C, 150°C, 180°C, 190°C, and 210°C for one hour in a heat-treatment furnace. Change in transmittance of the thin film was measured by a visible-UV spectrophotometer (Shimadzu UV 2450). The normal PET film was similarly heat treated, and the two films (silica-coated PET and normal PET) were compared.

2.3. Observation of Surface and Cross Section of Thin Film

The surface state of the excimer-light-treated film was observed by optical microscope (Kyowa Riken ME-LUX2), laser microscope (Olympus LEXT OLS4000), scanning electron microscope (Nihon Electronics JSM-7610F), and atomic-force microscope (Hitachi AFM-5100N). The cross section of the thin film (as a focused ion beam (FIB)-processed sample) was observed by transmission electron microscope (Hitachi H-9500).

3. Results

3.1. Formation and Cross-Sectional Structure of Dense SiO₂ Film Formed on PET by Excimer-Light Irradiation of PHPS Film

As an inorganic polymer with Si-N bonds, PHPS is soluble in a solvent. A di-butyl-ether solution (5 wt%) containing PHPS was spin-coated on PET to form a thin film, which was then irradiated with light at 100°C by using an excimer lamp (irradiation intensity: 42 mW/cm²; irradiation time: 2 min.). In this way, a dense silica film can be formed. Silica thin films were formed on both sides of the PET film. Cross-sectional TEM image of the PHPS-derived-SiO₂-coated PET film is shown in **Figure 1**. The SiO₂ thin film was uniformly formed on the PET at film thickness of approximately 55 to 60 nm. The thickness of this film is considered to be a result of minute irregularities on the surface of the PET. The surface of the SiO₂ film formed by applying the PHPS solution on PET was extremely flat, and no defects or the like were observed in the SiO₂ film.

The transparency of the thin film was very high; namely, the SiO₂-film-coated PET showed a transmission of 93% or more in the visible light region (400 - 800

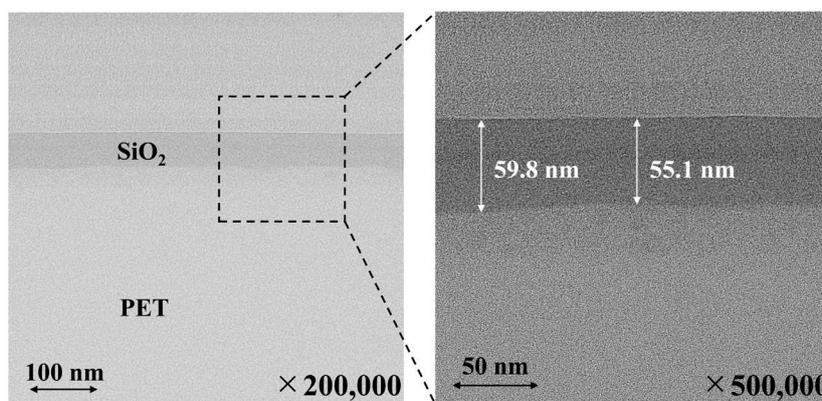


Figure 1. Cross-sectional TEM images of PHPS derived SiO₂ on PET.

nm). This transmission is better than that of the normal PET film (about 90%). Further, the adhesion strength of the thin film was evaluated by a JIS (Japan Industrial Standard) standard peeling tape test. In regard to the tape peeling test based on the JIS standard (JIS K5600), adhesion of the thin film was good, namely, 100/100 (remaining number/number of cuts).

In order to investigate heat resistance of the PET, change of surface condition and transmittance by varying heat-treatment temperature was examined by optical microscopy and absorption spectroscopy.

3.2. Change of Surface Condition and Transmittance by Varying Heat-Treatment Temperature

Optical micrographs of the change in the surface state due to the heat treatment (at each previously stated temperature) of the PET-only film and the PET coated with a SiO₂ film derived from PHPS are shown in **Figure 2**. As for the PET-only film, it was heat treated at 90 °C to 210 °C for one hour. No significant change in the surface state was observed up to 120 °C; however, the surface started becoming cloudy at 130 °C, and it became cloudy, and then it became significantly hazy at 180 °C or higher. In contrast, as for the thin-film-coated PET film, its transparency was maintained from 150 °C to 190 °C, and it only started to become hazy at 210 °C. However, the amount of haze due to heat treatment at 210 °C was significantly reduced compared to that in the case of the PET-only film.

Changes in the transmittance spectra for the films heat treated at each temperature are shown in **Figure 3**. As shown in **Figure 3(a)**, although PET-only shows a transmittance of about 90% in the visible light region (from 400 to 800 nm), the transmittance is greatly reduced as the heat-treatment temperature is increased. No change in transmittance was observed after heating at 90 °C while a slight decrease was observed after heating at 120 °C. The transmittance was

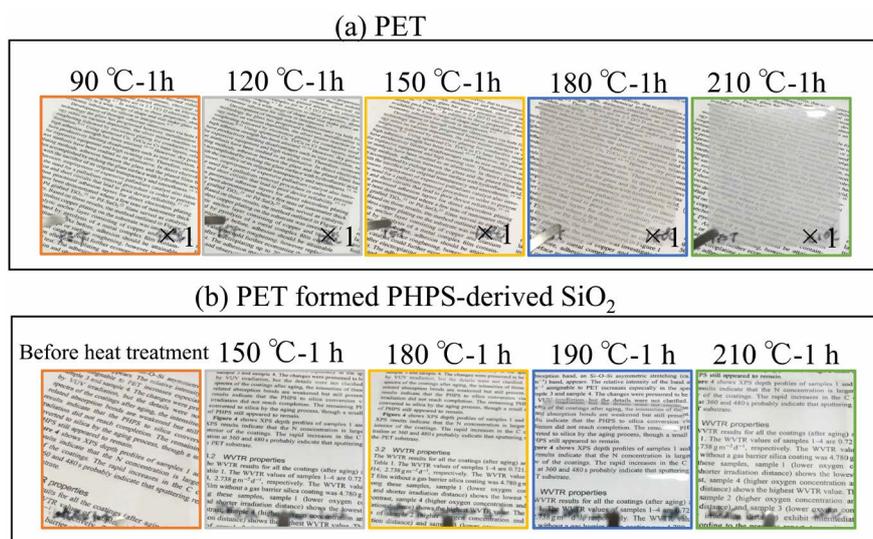


Figure 2. Optical microscope images of surface morphology of PET formed PHPS-derived SiO₂ and PET after heat treatment.

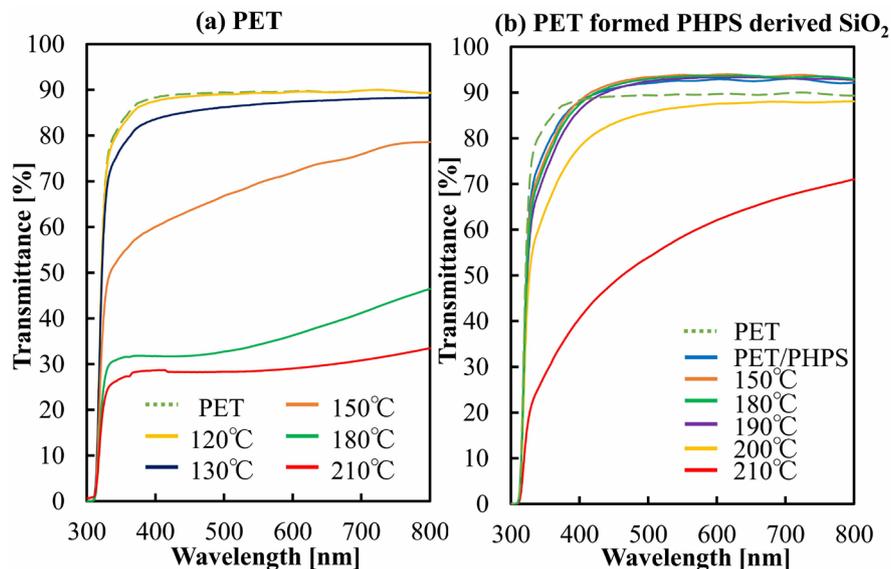


Figure 3. Comparison of transmittance spectra of PET formed PHPS-derived SiO₂ and PET after heat treatment.

greatly reduced after heating at 150°C, and after heating at 180°C to 210°C, it was about 30%. This change in transmittance corresponds to the degree of surface hazing at each heat-treatment temperature.

On the contrary, as shown in **Figure 3(b)**, the PET coated with a PHPS-derived SiO₂ film shows transmittance of about 92% to 93% at 400 to 800 nm, and it is slightly higher than that of the PET-only film. Below 400 nm, transmittance is reduced compared to that of the PET-only film. This reduced transmittance is considered to be explained as follows. The refractive index of the SiO₂ film formed on the upper layer (1.46) is lower than that of PET (1.56), and the reflectance is lowered at 400 to 800 nm due to the interference effect by light reflection at the film interface, and the reflectance is increased at 400 nm or less. This decrease in transmittance is negligible for heat treatment at 150°C to 190°C. At 200°C, transmittance starts to decrease (by several percents or so), and at 210°C, the extent of the decrease becomes larger (approximately 20%). However, the amount of decrease is significantly lower than that for heat treatment of the PET-only film at 180°C and 210°C (approximately 60%). These results indicate that the heat resistance of the SiO₂-thin-film-coated PET up to temperatures of about 180°C to 190°C is significantly improved.

The deterioration of PET films by heat treatment is due to the microstructural surface condition, therefore microstructural observation by Scanning Electron Microscope (SEM), Atomic-Force Microscope (AFM) and laser microscope was performed.

3.3. Microstructural Observations of Surface Condition

Enlarged observation images (Optical Microscope; OM: ×1000 and Scanning Electron Microscope; SEM: ×2000) of the surface of the SiO₂-film-coated PET

and the PET-only film obtained by optical microscope (OM) and SEM are compared in **Figure 4** and **Figure 5**. The surface of the PET only is very smooth and uniform (**Figure 4(a)** “Before”); however, after it was heat treated at 150°C, particles were deposited on the surface. As the processing temperature increased (to 180°C and 210°C), the size of the precipitated particles increased while their number increased. In the SEM micrographs shown in **Figure 5(a)**, particles with size of about 1 μm precipitated at 150°C become larger (about 2 to 4 μm) at 180°C, and particles with size of several microns or more are observed at 210°C. It is considered that light is irregularly reflected from the surface on which particles were deposited, so the surface appears white and hazy. These precipitated particles are understood to be low-molecular-weight cyclic oligomers of PET produced during synthesis of PET [15] [16]. It is considered that as the temperature rises, the oligomers present inside the PET move to the surface and crystallize there.

On the contrary, such precipitation of particles is not observed in the case of the PHPS-derived-SiO₂-film-coated PET (**Figure 5(b)**). Even for the heat treatment at 180°C, the surface was smooth and did not change compared to that before the heat treatment. As for the heat treatment at 210°C, a white-foggy-lined surface state is observed. This surface observation by SEM appears to correspond to the linear cracks observed in the OM image in **Figure 4(b)** 210°C. However, unevenness on the outermost surface was not observed; that is, the surface was in a relatively smooth state. The OM images obtained by transmitted light can obtain information about the interior of the film at best; however, the SEM can obtain information about the outermost surface. In view of that fact, it is supposed that the linear precipitates observed in the heat-treated film at 210°C are deposited at the interface between the PET and SiO₂ film. To confirm that supposition, the surface roughness was observed by laser microscope. Laser-microscope

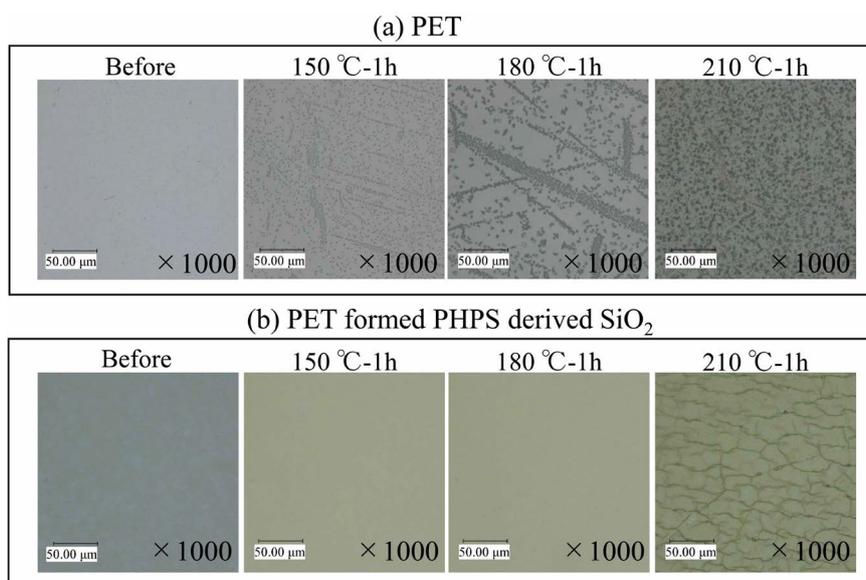


Figure 4. Optical microscope images of surface morphology after heat treatment.

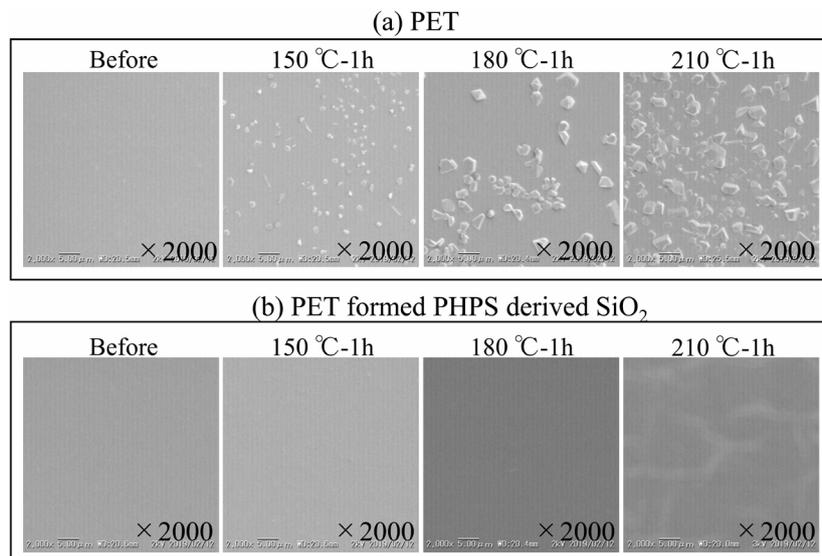


Figure 5. SEM images of surface morphology after heat treatment.

images of surface morphology before and after heat treatment are shown in **Figure 6**. As for the PET-only film (**Figure 6(a)**), irregularities start to appear on the surface at 150°C, and at 180°C, a number and large surface irregularities (due to growth of particles) are observed. At 210°C, surface irregularities cover the entire surface.

On the contrary, as for the PHPS-derived SiO₂-film-coated PET (**Figure 6(b)**), no surface unevenness is observed up to 180°C, and very few precipitates are observed at 190°C. Although the number of precipitates increases at 210°C, the surface irregularities are very few compared to those on the PET-only surface. This result indicates that 1) the heat resistance of the PHPS-derived-SiO₂-film-coated PET is very high compared to that of PET only and 2) the surface stays relatively flat even after heat treatment at 210°C. It is also understood from the above results that the cracks observed by OM are due to precipitation of linear precipitates near the interface between the PET and SiO₂.

To investigate finer areas of the surface morphology by heat treatment of the SiO₂-film-coated PET, the film was observed by AFM. The AFM images are shown in **Figure 7**. The SiO₂-thin-film-coated PET is smoother than the PET-only film (PHPS/PET: Ra = 0.276 nm versus PET: Ra = 0.669 nm). This result is explained by the fact that the unevenness of the PET surface was smoothed by the application of PHPS. When this SiO₂-coated PET film was heat treated at 150°C, particles on the surface grew slightly, resulting in Ra of 0.437 nm. After that, the films were heat treated at 180°C (Ra = 0.356 nm), 190°C (Ra = 0.311 nm), and 210°C (Ra = 0.443 nm); however, Ra of the film surfaces showed the value less than 0.5 nm, indicating smoothness of surface even after heat-treatment.

Film thickness and the interface state between SiO₂ and PET after heat treatment (210°C) were observed with cross-sectional transmission electron microscopy (TEM) so as to investigate the cause of deterioration.

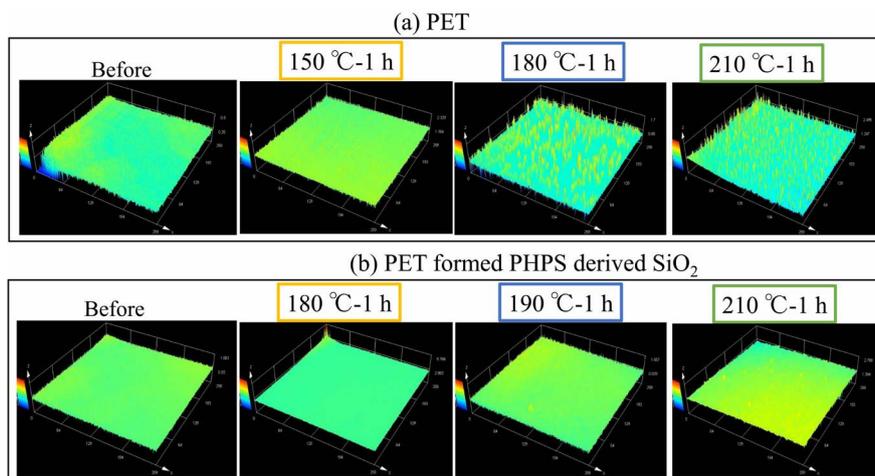


Figure 6. Laser microscope images of surface morphology after heat treatment.

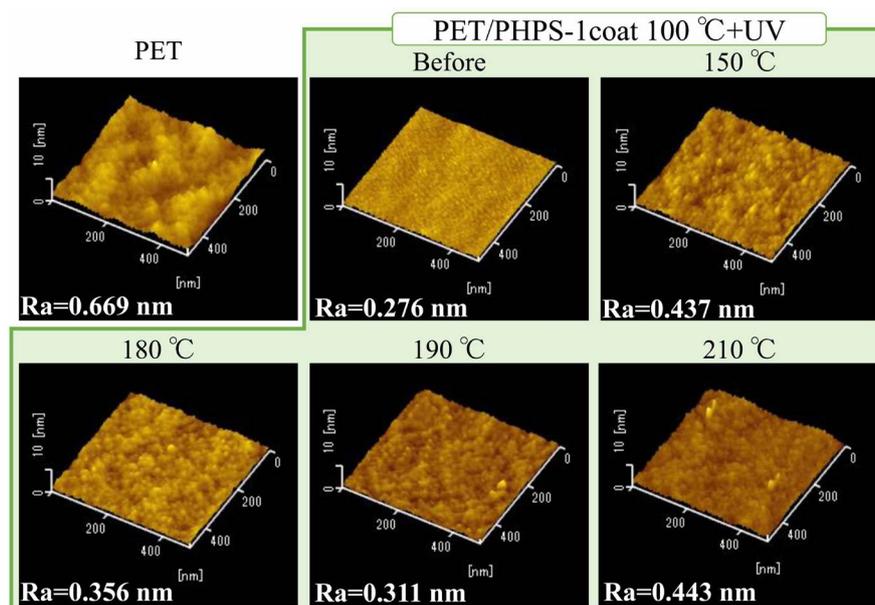


Figure 7. AFM images of surface morphology after heat treatment.

3.4. Cross-Sectional Observation after Heat Treatment (210°C) of PHPS-Derived SiO₂-Film-Coated PET

A cross-sectional TEM image of the SiO₂-film-coated PET film heat treated at 210°C for one hour is shown in **Figure 8**. Undulations in the PET film after the heat treatment are observed ($\times 25,000$ image). However, even after the heat treatment, thickness of the SiO₂ film on the PET was 55 to 60 nm, which is not significantly different from that before the heat treatment. A significant change from the state before the heat treatment is that a layer (with thickness of 20 to 30 nm) with different contrast is observed at the interface between the PET and the SiO₂ film ($\times 300,000$ image). This layer is supposed to be precipitates of low-molecular-weight oligomers originated from the PET. The precipitates are partially deposited at the surface in a manner that they pierce the SiO₂ film when

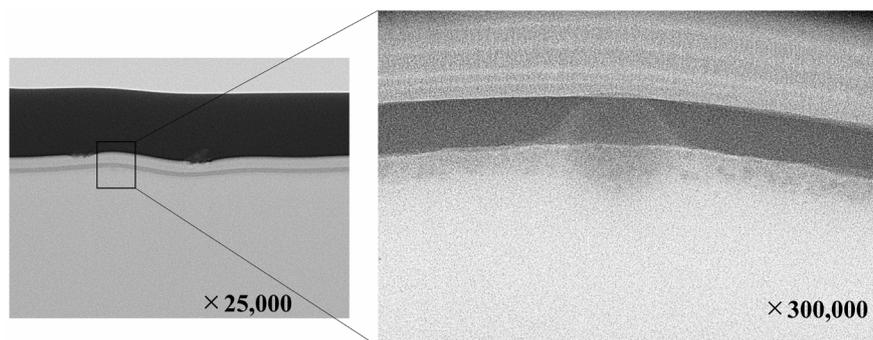


Figure 8. Cross-sectional TFM images of PHPS derived SiO₂ on PET after heat treatment at 210°C.

they grow. However, most of the precipitates remain at the interface between the PET and SiO₂ film. It is supposed that the surface precipitation was hardly observed in the surface observation by SEM and the surface was relatively smooth due to the fact that the SiO₂ surface is flat (because particles precipitate at the PET-SiO₂ interface). The cracked state of the surface observed by OM may be due to the particles deposited at the interface. The dense SiO₂ film formed on the PET suppresses the surface deposition of the oligomers, suggesting that it is effectively prevents whitening of the PET and improves the heat resistance of the PET. It is noteworthy that the heat resistance of PET can be significantly enhanced by forming a thin, dense SiO₂ film on the surface of PET (which inherently has low heat resistance).

4. Discussion

Although the mechanism by which a PHPS film is converted to a SiO₂ film by light irradiation at low temperature has been reported elsewhere [12], it is restated simply as follows. The outline of the method is shown in **Figure 9**. Polysilazane has strong absorption in the ultraviolet region (wavelength of 260 nm or less), and it absorbs the vacuum UV light (wavelength of 172 nm, which is the emission wavelength of excimer lamp). The energy of the excimer lamp with that emission wavelength (172 nm) corresponds to 166 kcal/mol. On the contrary, the binding energies of the Si-N, Si-H, and N-H bonds of polysilazane are 105, 71, and 92 kcal/mol, respectively. The energy of ultraviolet light is greater than those binding energies, so it is sufficient to break the polysilazane bonds. The broken bonds are instantaneously oxidized and converted to SiO₂ by reactive oxygen species such as ozone (O₃) and singlet oxygen (O(¹D))) generated by absorption of UV light by a small amount of oxygen (20 - 30 ppm) existing in nitrogen gas or in the chamber of the light-irradiation apparatus. It is therefore possible to form a dense SiO₂ film even at low temperature.

The formed SiO₂ film is smooth and dense. The dense SiO₂ film formed on PET prevents the low-molecular-weight oligomers present in the PET film precipitating on the PET surface, thereby improving heat resistance of the PET. The cause of thermal deterioration of PET is said to be that low-molecular-weight

diating a PHPS film with excimer light) were investigated. The SiO₂ film formed by excimer light irradiation was dense and uniform with thickness of 55 to 60 nm. Compared with a normal PET film, which is deteriorated and whitened by heat treatment at about 110°C - 120°C, the developed SiO₂-coated PET film maintains its transparency—even when heat treated at 180°C to 190°C for one hour—and does not deteriorate. This strong heat resistance is considered to be due to the fact that the dense SiO₂ film formed on the PET surface prevents surface precipitation and crystallization of low-molecular-weight oligomers (which cause thermal degradation of PET). It is expected that by enhancing the heat-resistance temperature of PET (with high versatility and low cost) to about 180°C to 190°C, in this manner, it will be possible to apply a PET film as a substrate for flexible devices. Next step, in order to enhance heat resistance of the film at higher temperature, we are planning to vary photo intensity of excimer light and irradiation time because photo intensity and irradiation time affect film quality of the SiO₂ film.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Wong, W.S. and Salleo, A. (2009) *Flexible Electronics: Materials and Applications*. Springer, New York. <https://doi.org/10.1007/978-0-387-74363-9>
- [2] White, M.S., Kaitenbrunner, M., Istrokowacki, E.D., Gutnichenko, K., Kettlgruber, G., Graz, I., Aazou, S., Ulbricht, C., Egbe, D.A.M., Miron, M.C., Major, Z., Schaber, M.C., Sekitani, T., Someya, T., Bauer, S. and Sariciftci, N.S. (2013) Ultrathin Highly Flexible and Stretchable PLEDs. *Nature Photonics*, **7**, 811-816. <https://doi.org/10.1038/nphoton.2013.188>
- [3] Sekitani, T. and Someya, T. (2011) Human-Friendly Organic Integrated Circuit. *Materials Today*, **14**, 398-407. [https://doi.org/10.1016/S1369-7021\(11\)70184-5](https://doi.org/10.1016/S1369-7021(11)70184-5)
- [4] Sekitani, T., Zschieschang, U., Klauk, H. and Someya, T. (2010) Flexible Organic Transistor and Circuits with Extreme Bending Stability. *Nature Materials*, **9**, 1015-1022. <https://doi.org/10.1038/nmat2896>
- [5] Nomura, K., Ohta, H., Kamiya, T., Hirano, M. and Hosono, H. (2004) Room-Temperature Fabrication of Transparent Flexible Thin-Film Transistors Using Amorphous Oxide Semiconductors. *Nature*, **432**, 488-492. <https://doi.org/10.1038/nature03090>
- [6] Sekitani, T. and Someya, T. (2010) Stretchable Large-Area Organic Electronics. *Advanced Materials*, **22**, 2228-2246. <https://doi.org/10.1002/adma.200904054>
- [7] Motomura, G., Nakajima, Y., Nakata, M., Takei, T., Yamamoto, T., Kurita, T. and Shimizu, N. (2014) Flexible Organic Light Emitting Diode Display on an Ultra-Thin Polyimide Film. *The Journal of the Institute of Electronics, Information and Communication Engineers C*, **J97-C**, 61-68.

- [8] Nakajima, Y., Fujisaki, Y., Takei, T., Sato, H., Nakata, M., Suzuki, M., Fukagawa, H., Motomura, G., Shimizu, T., Isogai, Y., Sugirani, K., Katoh, T., Tokito, T., Yamamoto, T. and Fujikake, H. (2011) Low Temperature Fabrication of 5-in QVGA Flexible AMOLED Display Driven by OTFTs Using Olefin Polymer as the Gate Insulator. *Journal of the Society for Information Display*, **19**, 861-866.
- [9] Park, J., Kim, T., Stryakhilev, D., Lee, D., Mo, Y.G., Jin, D. and Chung, H.K. (2009) Flexible Full Color Organic Light-Emitting Diode Display on Polyimide Plastic Substrate Driven by Amorphous Indium Gallium Zinc Oxide Thin-Film Transistor. *Applied Physics Letters*, **95**, Article ID: 013503. <https://doi.org/10.1063/1.3159832>
- [10] Chien, C., Wu, C., Tsai, Y., Kung, Y., Lin, C., Hsu, P., Hsieh, H., Wu, C., Yeh, Y., Leu, C. and Lee, T. (2011) High Performance Flexible a-IGZO TFTs Adopting Stacked Electrodes and Transparent Polyimide-Based Nanocomposite Substrate. *IEEE Transactions on Electron Devices*, **58**, 1440-1446. <https://doi.org/10.1109/TED.2011.2109041>
- [11] Imamura, Y., Takeda, K. and Nitta, A. (2019) An Improvement of Homogeneity for Organic Transparent Conductive Film Prepared by Inkjet Printing. *The Journal of the Institute of Electronics, Information and Communication Engineers C*, **J102-C**, 77-85.
- [12] Ohishi, T., Sone, S. and Yanagida, K. (2014) Preparation and Gas Barrier Characteristics of Polysilazane-Derived Silica Thin Films Using Ultraviolet Irradiation. *Materials Sciences and Applications*, **5**, 105-111. <https://doi.org/10.4236/msa.2014.53015>
- [13] Ohishi, T., Yamazaki, Y. and Nabatame, T. (2016) Preparation, Structure and Gas Barrier Characteristics of Polysilazane-Derived Silica Thin Film Formed on PET by Simultaneously Applying Ultraviolet-Irradiation and Heat-Treatment. *Frontiers in Nanoscience and Nanotechnology*, **2**, 149-154. <https://doi.org/10.15761/FNN.1000126>
- [14] Ohishi, T. and Yanagida, K. (2016) Preparation and Gas Barrier Characteristics of Polysilazane-Derived Multi-Layered Silica Thin Films Formed on Alicyclic Polyimide Film Using Ultraviolet Irradiation. *Frontiers in Nanoscience and Nanotechnology*, **2**, 173-178. <https://doi.org/10.15761/FNN.1000131>
- [15] Cimecioglu, A.L., Zeronian, S.H., Alger, K.W., Collins, M.J. and East, G.C. (1986) Properties of Oligomers Present in Poly(Ethylene Terephthalate). *Journal of Applied Polymer Science*, **32**, 4719-4733. <https://doi.org/10.1002/app.1986.070320436>
- [16] Yamanaka, Y., Kitagawa, J., Kojima, K. and Nakano, H. (2018) Precipitation Phenomena of Cyclic Oligomers on the Surface of PET Film Laminated Steel Sheet during Wet-Heat Treatment. *Journal of the Surface Finishing Society of Japan*, **69**, 302-307.