

# Ceramic Thin Films on Plastics: A Versatile Transfer Process for Large Area as Well as Patterned Coating

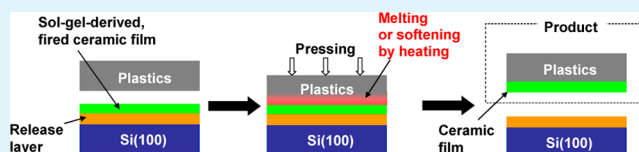
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## S Supporting Information

**ABSTRACT:** A versatile technique for fabricating ceramic thin films on plastics has been proposed. The technique comprises (i) the deposition of a gel film by spin- or dip-coating on a silicon substrate coated beforehand with a release layer, (ii) the firing of the gel film into a ceramic film, and (iii) its transfer onto plastics by melting or softening the plastics surface. Reflective anatase and electrically conductive indium–tin-oxide (ITO) thin films were prepared on acrylic resin and polycarbonate substrates. Patterned ITO thin films could also be fabricated on plastics by using a mother silicon substrate with periodic grooves.

**KEYWORDS:** coating, thin films, ceramics, plastics, flexible electronics, sol–gel



## INTRODUCTION

A versatile technique that realizes large area ceramic thin films on plastics is a challenge in technologies on flexible electronic devices and for those aiming at the replacement of glass substrates by lightweight plastics.<sup>1–22</sup> Such ceramic thin films should be in crystalline and densified (less porous) states so that they have superior functions such as electronic conduction, piezoelectricity and optical reflectivity. However, both crystallization and densification (sintering) need atomic diffusion, which is activated at high temperatures greater than 500 °C. In other words, ceramic thin films are the most functionalized when they are “fired.” Thin films deposited on plastics, however, cannot be fired because the plastics cannot survive at such high temperatures.

This is why “low-temperature” processing has been focused on since 1970s<sup>2–4</sup> for realizing ceramic thin films on plastics.<sup>1–22</sup> The greatest efforts have been made on vapor phase depositions, which include sputtering,<sup>3,5</sup> chemical vapor deposition (CVD),<sup>6</sup> atomic layer deposition,<sup>7</sup> electron-<sup>8</sup> and ion-beam<sup>9</sup> deposition, ion-plating,<sup>4,10</sup> pulsed laser deposition,<sup>11</sup> reactive plasma deposition<sup>12</sup> and thermal evaporation.<sup>2,13</sup> In such vapor phase depositions, crystallization may be achieved basically by high activities of atomic and molecular species in vapor phase as well as on the substrate surface. However, even in these techniques, post-treatments are needed in some cases to improve crystallinity; hydrothermal treatment for atomic layer deposited titania thin films is an example.<sup>14</sup> Liquid phase deposition (LPD) is another technique,<sup>15</sup> but dense film formation cannot be expected because it is based on precipitation of crystals from aqueous solutions. Deposition of crystalline oxide nanoparticles by spin- and dip-coating is another technique,<sup>16,17</sup> but a firing process for sintering is needed when porosity is to be eliminated. As far as titania thin films are concerned, crystalline, spongelike, or mesoporous thin

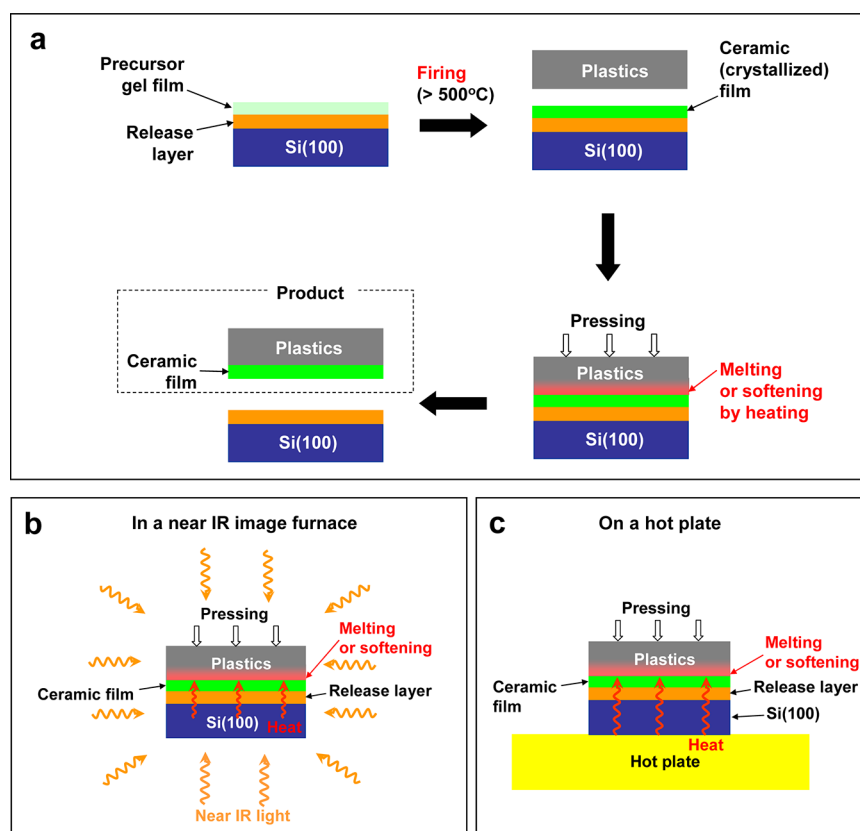
films are reported to be formed from alkoxide solutions at temperatures lower than 90 °C under specific chemical conditions.<sup>18,19</sup> Several techniques have also been proposed to crystallize sol–gel-derived amorphous gel films on plastics without firing.<sup>20–22</sup> The exposure to laser beams<sup>20</sup> and humid vapors<sup>21</sup> and the soaking in hot water<sup>22</sup> are reported to induce crystallization of gel films. However, neither high crystallinity nor high density (low porosity) is expected because of the low processing temperatures, which limit the atomic diffusion for crystal growth and densification.

Here we propose a new technique that realizes ceramic thin films on plastics based on a sol–gel technique and a transfer process. The technique comprises (i) the deposition of a polymer release layer and a precursor gel film by spin- or dip-coating on a thermally resistant silicon substrate, (ii) the firing of the gel film to convert it into a dense, crystalline metal oxide film, and (iii) the transfer of the crystalline film onto a plastic substrate by melting or softening the surface of the plastic substrate. The technique proposed here has three significant points. (a) The “firing” process guarantees the crystallization and densification of films. (b) Large area as well as patterned coating can be achieved without any specialized equipment. (c) The technique is applicable regardless of the combinations of ceramics and plastics, and hence is versatile. The authors have recently proposed a transfer process where adhesives are used to transfer sol–gel-derived ceramic thin films onto plastic substrates.<sup>23,24</sup> In that technique, an adhesive layer is present between the ceramic film and the plastic substrate. On the other hand, the technique proposed here allows direct bonding between the ceramic film and the plastic substrate without any

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**Figure 1.** Illustration of the process of the technique. (a) Whole process. A polymer release layer and a metal oxide precursor gel film are deposited by spin- or dip-coating on an Si(100) substrate. The precursor gel film is fired at temperatures over 500 °C to be converted into a crystalline metal oxide film, which is then transferred onto a plastic substrate under pressing by melting or softening the surface of the plastic substrate. In some cases, the release layer is left on the surface of the transferred ceramic thin film, and such a layer can easily be removed using a cellophane adhesive tape. (b) Softening the plastic substrate surface in a near-infrared image furnace, where the Si(100) substrate absorbs the near-infrared light and radiates the heat, which is transferred to the plastic substrate. (c) Softening the plastic substrate surface using a hot plate, where the heat is conducted from the Si(100) substrate side to the plastic substrate.

substances in between. We demonstrate in this letter the availability of the technique, showing the results on optically reflective anatase and transparent, electrically conductive indium–tin-oxide (ITO) thin films on plastics including acrylic resin (polymethylmethacrylate, PMMA) and polycarbonate (PC) substrates. One may realize that the transferred ceramic thin films have flat and smooth surface and interface without cracks although ceramics are brittle materials and the transfer process seems severe for such a thin ceramic film to survive. Patterned ceramic thin films on plastics are also demonstrated to be fabricated by using a mother silicon substrate with periodically etched surface.

## EXPERIMENTAL SECTION

**Preparation of the Release Layers.** Figure 1a shows the process of the technique. First the release layers were prepared on Si(100) substrates in the following manner. N-methyl-2-pyrrolidone solution of polyamic acid (20 mass%, U-Varnish-S, Ube Industries, Ube, Japan), polyvinylpyrrolidone (PVP K15, 10000 in viscosity average molecular weight, Tokyo Kasei Kogyo Co., Tokyo, Japan) and 1-methyl-2-pyrrolidone (Wako Pure Chemical Industries, Osaka, Japan) were used as the starting materials for preparing the polyimide (PI)-PVP mixture release layers. Solutions of mass ratios, U-Varnish-S:PVP:1-methyl-2-pyrrolidone = 6:1:2 and 10:1:2, were used for preparing the release layers for anatase and ITO thin films, respectively. Spin-coating was conducted on Si(100) substrates at a spinning rate of 8000 rpm, followed by heating at a rate of 10 °C min<sup>-1</sup> up to 120 °C and keeping there for 60 min. Further heat treatment was conducted at 150 °C for

30 min, at 250 °C for 20 min, and at 450 °C for 10 min in this sequence, where the films were heated at 10 °C min<sup>-1</sup> between different temperatures.

**Preparation of Anatase and ITO Thin Films on the Release Layers.** Anatase and ITO thin films were prepared on the release layers. Anatase thin films were prepared on the release layers from a solution of mole ratios, Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>:H<sub>2</sub>O:HNO<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH = 1:1:0.2:20, where Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, nitric acid (69–70%) and ethanol, all purchased from Wako Pure Chemical Industries, and ion-exchanged water were used as the starting materials. Titania gel films were prepared on the release layers by spin-coating at 8000 rpm, followed by heating at 5 °C min<sup>-1</sup> up to 600 °C in an electric furnace.

ITO thin films were prepared on the release layers using In(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O, SnCl<sub>2</sub>·2H<sub>2</sub>O, acetylacetone, ethylene glycol, polyethylene glycol (PEG 2000), and 1-methoxy-2-propanol and methanol, all purchased from Wako Pure Chemical Industries. A starting solution of mole ratios In(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O:SnCl<sub>2</sub>·2H<sub>2</sub>O:CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>:HOCH<sub>2</sub>CH<sub>2</sub>OH:PEG 2000:CH<sub>3</sub>OCH<sub>2</sub>CH(OH)CH<sub>3</sub>:CH<sub>3</sub>OH = 0.9:0.1:0.45:1.8:8.5 (monomer equivalent):6.2:17.4 was prepared by the following procedure. First, In(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O was dissolved in the mixture of HOCH<sub>2</sub>CH<sub>2</sub>OH and CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>, followed by heating at 90 °C for 3 h. The mixture of CH<sub>3</sub>OH and CH<sub>3</sub>OCH<sub>2</sub>CH(OH)CH<sub>3</sub> was added to the solution, and then SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved, followed by heating at 90 °C for 2 h. PEG 2000 was added to the solution, and heated at 90 °C for 30 min, resulting in a yellow, transparent coating solution. Spin-coating was conducted on the release layers on Si(100) substrates at 8000 rpm, followed by firing at 500 °C for 10 min in an electric furnace. The spin-coating and the firing were repeated eight times.

### Transfer of the Fired Thin Films onto Plastic Substrates.

Finally the anatase and ITO thin films prepared on the release layers were transferred onto plastic substrates (Figure 1a). In the transfer process, the ceramic thin film is made contact with the plastic substrate surface under a load to make a plastics/ceramic-film/release-layer/silicon stack. Then the plastic substrate surface that is in contact with the ceramic film is molten or softened by heat under a load. The molten or softened surface of plastics acts as an adhesive, and the polymer release layer enables the fired ceramic film to be detached from the silicon substrate.

The melting or softening of the whole plastic substrate should be avoided in the transfer process, which can be achieved by irradiating the plastics/ceramic-film/release-layer/silicon stack with near-infrared (IR) light in a near-IR image furnace (Figure 1b) or by heating the stack from the silicon substrate side on a hot plate (Figure 1c). In a near-IR image furnace, only the silicon substrate absorbs the near-IR light<sup>25</sup> and radiates the heat, which is transferred to the plastic substrate (Figure 1b). When the stack is placed on a hot plate, the heat is conducted from the silicon substrate side to the plastic substrate (Figure 1c). In either case, the surface of the plastic substrate can be molten or softened without damaging the substrate by optimizing the heating rate and temperature.

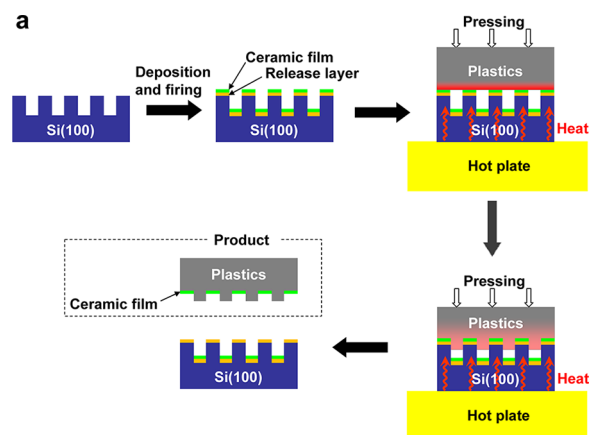
The fired anatase thin films were transferred onto PMMA and PC substrates using a near-IR image furnace (MLA3000-P-N, ULVAC-RIKO, Kanagawa, Japan) where the plastics/TiO<sub>2</sub>/release-layer/Si(100) stacks bound with binder double clips were heated up to 170 °C. The heating rates were 50 and 75 °C min<sup>-1</sup> for the transfer onto 5 mm thick PMMA and PC substrates, respectively.

The fired ITO thin films were transferred onto PC substrates using a hot plate. The ITO/release-layer/Si(100) sample was placed on a hot plate where the rear side of the Si(100) substrate was in contact with the hot plate. The PC substrate was fixed on a copper block with a double-sided adhesive tape, mounted on the heated ITO/release-layer/Si(100) sample, and kept there for a prescribed period of time under a unidirectional pressure of 2.1 MPa by the copper block. The PC/ITO/release-layer/Si(100) stacks including 0.5 and 5 mm thick PC substrates were placed on the hot plate of 200 °C for 5 s and 220 °C for 2.5 min, respectively. After that, the stack was removed from the hot plate, and cooled in the ambient atmosphere. The fired ITO films were transferred on 5 mm thick PC substrates also in the near-IR image surface, where the PC/ITO/release-layer/Si(100) stacks bound with binder double clips were heated at 75 °C min<sup>-1</sup> up to 200 °C. The release layer left on the surface of the transferred ITO thin film was removed by a cellophane adhesive tape.

### Preparation of Patterned ITO Thin Films Plastic Substrates.

Figure 2 illustrates the process for preparing patterned ITO thin films on plastics. Periodic grooves 50 μm in width and 100 μm in depth were made on Si(100) substrates by dry etching that was conducted by Silicon Sensing Systems Japan, Ltd., Amagasaki, Japan. The release layer was deposited by dip-coating at a substrate withdrawal speed of 1 cm min<sup>-1</sup>, where the withdrawal direction was parallel to the grooves, followed by the heat treatment under the conditions mentioned above. The precursor gel film was deposited by dip-coating on the release layer, followed by firing to convert the gel film into an ITO film under the same condition described above. The fired ITO thin film was transferred onto a 0.5 mm thick PC substrate by placing the PC/ITO/release-layer/Si(100) stack on a hot plate of 200 °C for 10 s under a unidirectional pressure of 4.2 MPa. The release layer left on the surface was removed by a cellophane adhesive tape.

**Measurements and Observations.** The ceramic thin films on plastic substrates were observed by an optical microscope (KH-1300, HiROX, Tokyo, Japan), a field-emission scanning electron microscope (FE-SEM) (JSM-6500F, JEOL, Tokyo, Japan) and an SEM (JSM-6510, JEOL, Tokyo, Japan). The cross section for the SEM observation was fabricated by focused ion beam (FIB) machining, which was conducted by Foundation for Promotion of Material Science and Technology of Japan, Tokyo, Japan, by the following manner. A carbon layer was deposited on the surface of the sample using an auto carbon coater (JEC-570, JEOL). The sample was introduced in an FIB instrument (StrataDB235M, FEI, Hillsboro,



**Figure 2.** Process for preparing patterned ceramic thin films on plastic substrates. The release layer and the precursor gel film are deposited by dip- and spin-coating on Si(100) substrates with periodic grooves, respectively, followed by firing to convert the gel film into a ceramic film. The plastics/ceramic-film/release-layer/Si(100) stack is placed on a hot plate under a load, where the plastic substrate surface in contact with the ceramic film is molten or softened, and thus the transfer of the ceramic film onto the plastic substrate is realized.

U.S.A.), and a platinum layer was deposited by sputtering. Both carbon and platinum layers were the protective layers for the FIB machining. Then the sample was cooled down to -165 °C, and cross section was fabricated with Ga<sup>+</sup> ions with a tilting angle and acceleration voltage of 0–2° and 30 kV, respectively, and with ion currents of 5200 and 80 pA for the initial and final stages, respectively. For the patterned ITO thin films on the PC substrate, a cut was made with a surgical knife before SEM observation in order to improve the visibility of the surface roughness. Scanning probe microscopic observation was made using Nanopics 1000, Seiko Instruments, Inc., Chiba, Japan.

Optical absorption spectra were measured on the samples using an optical spectrometer (V-570, JASCO, Tokyo, Japan), where the reference was air. Reflection spectra were recorded using the same spectrometer with a reflection attachment (SLM-468, JASCO). Infrared absorption spectra were measured for the release layers that were deposited on Si(100) substrates with or without ceramic thin films. The spectra were measured using a Fourier transform-IR spectrometer (FT/IR 4100, JASCO), where an Si(100) substrate was used as the reference. X-ray-diffraction (XRD) patterns were obtained on the thin film samples by ordinary 2θ/θ mode using an X-ray diffractometer (Rint 2550 V, Rigaku, Tokyo, Japan) with Cu Kα radiation operated at 40 kV and 300 mA.

The electrical resistance of the ITO film on plastics was measured by four-point probe method using a digital multimeter (7555, Yokogawa Electric Co., Tokyo, Japan) equipped with a four-point probe (MCP-TP06, Mitsubishi Chemical Analytech Co., Mie, Japan). The volume resistivity  $\rho_v$  was calculated from the measured resistance  $R$ , the thickness  $t$  determined from the SEM cross-section, and resistivity correction factor  $f$ , by  $\rho_v = Rtf$ .

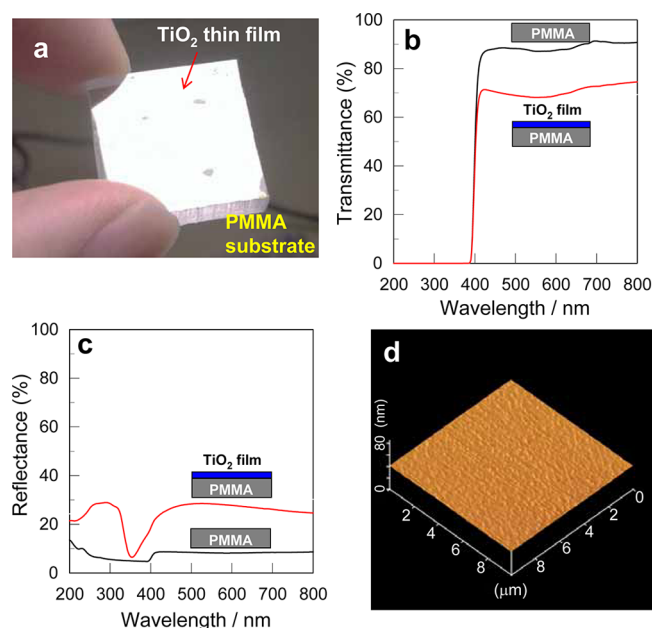
## RESULTS AND DISCUSSION

The release layers had smooth surface as is shown in the surface roughness data given in the Supporting Information (Figure S1). As is demonstrated in the IR absorption spectra (Supporting Information, Figure S2), the release layers with ceramic thin film overlayers were resistant even when heated at 500 °C while they were decomposed when heated up to 600 °C. However, even when heated at 600 °C, small absorption bands were detected at 1050 and 1600 cm<sup>-1</sup>, which may be due to vibrations in decomposition residues. Such release layers, organic polymers or their decomposition residues, allowed the ceramic thin films to be detached from the Si(100) substrates



where the release layers and the ceramic thin films are thought to be just weakly bonded via van der Waals interaction or hydrogen bonds. When heated at higher temperatures or for longer periods of time, the release layers were totally decomposed, and as a result the ceramic thin films were too strongly bonded to the Si(100) substrates to be detached possibly due to the Si–O–metal covalent bond formation.

Figure 3a shows a 60 nm thick TiO<sub>2</sub> thin film on a 5 mm thick PMMA substrate prepared by the proposed technique.



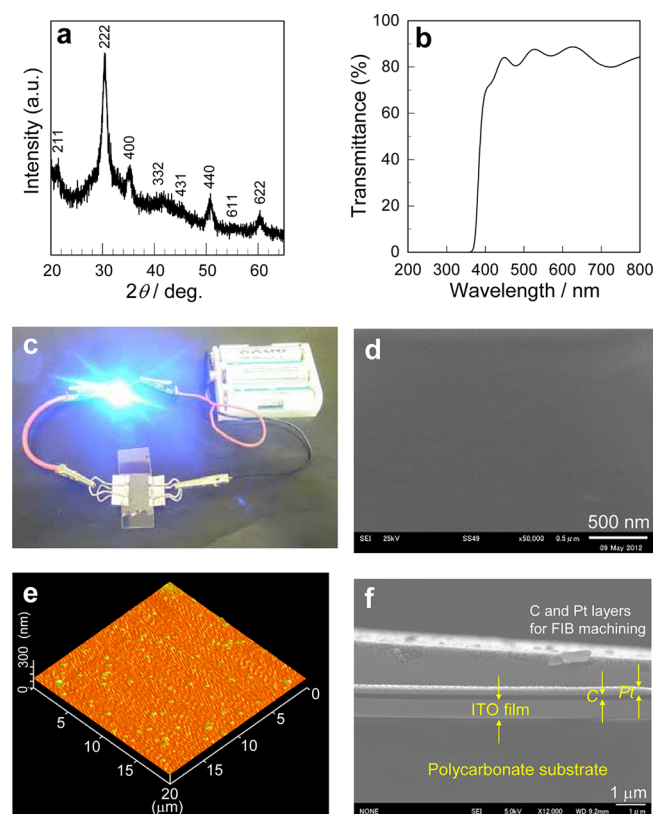
**Figure 3.** (a) Appearance, (b) absorption spectra, (c) reflection spectra, and (d) scanning probe microscopic surface image of the 60 nm thick anatase films on 5 mm thick PMMA and PC substrates. The substrates were (a–c) PMMA and (d) PC. The transfer was conducted in the near-IR image furnace where the stack was heated up to 170 °C at (a–c) 50 and (d) 75 °C min<sup>-1</sup>. The absorption spectra were measured with a bare PMMA substrate as the reference in b. Spectra are also given for a bare PMMA substrate in b and c.

Although a single layer anatase film showed only a small anatase (101) peak due to the small thickness, a multilayer thicker anatase film exhibited clear anatase (101), (004), and (105) peaks in the XRD patterns as shown in Supporting Information, Figure S3. The surface of the sample looks white in Figure 3a because of the reflection of the white light by the anatase film. The optical transparency and the high reflectivity of the anatase film on the PMMA substrate are demonstrated in the optical absorption and reflection spectra, respectively (Figure 3b, c). These spectra were measured for the film on the PMMA substrate, and the reference was air for the absorption spectra measurements. The PMMA substrate with the anatase film exhibited lower transmittance than the bare substrate (Figure 3b), which is simply due to the high reflectivity of the anatase film (Figure 3c). The scanning probe microscopic image of the surface of the anatase film transferred on a 5 mm thick PC substrate (Figure 3d) demonstrates high smoothness with an  $R_a$  value as small as 0.62 nm; the surface roughness profile is also given in the Supporting Information (Figure S1b).

In the transfer process, the anatase film is bonded with the softened plastics surface under heating, and the film is detached from the Si(100) substrate after the plastic surface is cooled and solidified. The adhesion between the TiO<sub>2</sub> film and the PMMA

substrate may be realized via van der Waals interaction, which is thought to be strong enough to detach the film from the Si(100) substrate. It should be noted that the anatase films transferred on plastic substrates had no cracks and had flat and smooth surface although the transfer process seems severe for such thin ceramic thin films to survive.

Transparent and electrically conductive ITO thin films could also be prepared on plastic substrates. The crystallization via the repeated firing at 500 °C is evidenced in the XRD pattern of the film on a 5 mm thick PC substrate (Figure 4a). The film



**Figure 4.** (a) XRD pattern, (b) optical absorption spectra, (c) demonstration of electrical conductivity, (d) SEM surface image, (e) scanning probe microscopic surface image, and (f) SEM image of the cross-section for the 660 nm thick ITO films transferred on PC substrates. The thickness of the PC substrates was (a, b, f) 5 mm and (c–e) 0.5 mm. The transfer was conducted on a hot plate, where the PC/ITO/release-layer/Si(100) stack was placed on a hot plate at (a, b) 220 °C for 2.5 min and (c–e) 200 °C for 5 s for under a pressure of 2.1 MPa. For f, the transfer was conducted in the near-IR image furnace, where the stack was heated up to 200 °C at 75 °C min<sup>-1</sup>. Miller indices placed in (a) are those of ITO with bixbyite structure. The absorption spectra in (b) were measured using a bare PC substrate as a reference. The cross-section shown in (f) was made by FIB.

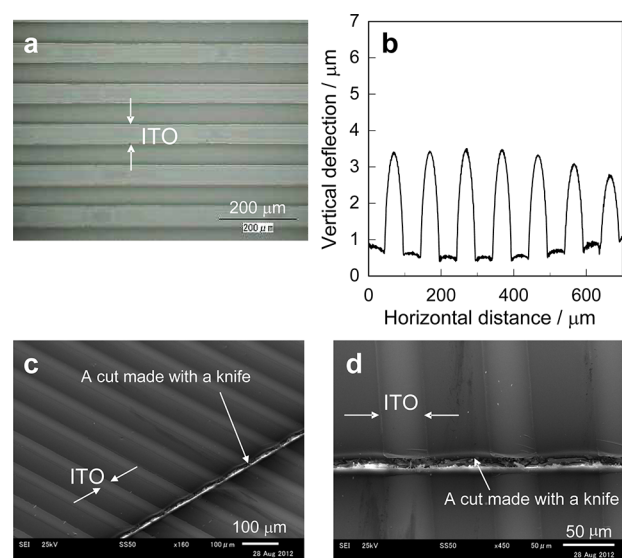
was transparent as is seen in the optical absorption spectra, which were measured on the PC substrate with air as the reference (Figure 4b). The absorption and reflection spectra measured at wavelengths up to 2000 nm are also given in the Supporting Information (Figure S4).

Figure 4c demonstrates the electrical conductivity of the ITO film on a 0.5 mm thick PC substrate, where an LED lamp is shining by an electric current through the film. The resistivity measured by four-point probe technique was  $8.69 \times 10^{-3} \Omega \text{ cm}$ , which are one order higher than those reported for ITO thin

films on plastic substrates fabricated by sputtering or pulsed laser deposition, i.e.,  $(5-7) \times 10^{-4} \Omega \text{ cm}$ .<sup>11,26,27</sup> The conductivity may be improved by optimizing the coating solution compositions as well as heat treatment conditions.

The flat and smooth surface of the ITO film on a 0.5 mm thick PC substrate is seen in the SEM image (Figure 4d) as well as in the scanning probe microscopic image (Figure 4e), where the  $R_a$  value was as small as 15 nm; the surface roughness profile is also given in the Supporting Information (Figure S1c). To observe the cross-section, focused ion beam (FIB) machining was conducted on an ITO film that was transferred to a 5 mm thick PC substrate in a near-IR image surface, where the PC/ITO-on-Si(100) stack was heated at  $75 \text{ }^\circ\text{C min}^{-1}$  up to  $200 \text{ }^\circ\text{C}$ . Figure 4f shows the SEM image of the cross section thus made, where carbon and platinum were deposited for protecting the sample in the FIB machining. The dense microstructure is seen in the cross-section of the ITO film, which was achieved by the firing process. High smoothness is confirmed for the film/substrate interface as well as for the film surface.

Patterned ITO thin films could also be prepared by the technique illustrated in Figure 2. The optical micrograph of the patterned ITO thin films thus prepared on a PC substrate is shown in Figure 5a. It is seen that ITO thin films  $50 \mu\text{m}$  in



**Figure 5.** (a) Optical micrograph, (b) surface roughness profile, (c) SEM image, and (d) magnified SEM image of the 0.5 mm thick PC substrate coated with the patterned ITO thin film. The transfer was conducted on a hot plate, where the stack was placed on a hot plate of  $200 \text{ }^\circ\text{C}$  for 10 s under a pressure of 4.2 MPa. The ITO thin films are present in the valleys in b. A cut was made with a surgical knife for c and d for improving the visibility of the surface roughness.

width are aligned parallel on the PC substrate. In the transfer process, the softened plastics slightly intrude into the grooves of the Si(100) substrate as is schematically illustrated in Figure 2. As a result, periodic PC ridges ca.  $3 \mu\text{m}$  in height were formed on the PC substrate as seen in the surface roughness profile shown in Figure 5b, where the ITO films are present in the valleys. However, such ridges and valleys are only slightly visible in the SEM pictures as shown in panels c and d in Figure 5 because of the small height of the ridges compared with their width. The height of the ridges can be controlled by controlling the heating rate, temperature, and load in the transfer process.

Transfer or lift-off techniques involving a “firing” step have been proposed recently by two research groups.<sup>28,29</sup> Qi et al.<sup>28</sup> prepared lead zirconate titanate (PZT) thin ribbons on polydimethylsiloxane (PDMS) rubbers. They prepared 500 nm thick PZT precursor thin films by radio frequency (rf) sputtering on prepatterned MgO substrates, followed by firing at  $750 \text{ }^\circ\text{C}$  to crystallize the PZT precursor films. The MgO substrates with the PZT ribbons were dipped in phosphoric acid, which undercut and loosened the ribbons. Then the PZT ribbons were transferred to PDMS plates by pressing and peeling off. Park et al.<sup>29</sup> prepared 300 nm thick  $\text{BaTiO}_3$  thin ribbons on Kapton films. They deposited amorphous  $\text{BaTiO}_3$  films with top Au electrodes on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates by rf magnetron sputtering, followed by firing at  $700 \text{ }^\circ\text{C}$ . After etching the Au/ $\text{BaTiO}_3$ /Pt layers in narrow bridge patterns by an inductive coupled plasma-reactive ion etcher, the underlying Si layer was removed by wet etching with tetramethylammonium hydroxide, which separated the Au/ $\text{BaTiO}_3$ /Pt ribbons from the mother substrate. After transferring the Au/ $\text{BaTiO}_3$ /Pt ribbons on a PDMS stamp, the ribbons were brought in contact with a polyurethane (PU)-coated Kapton film, and the PU layer was optically cured, leading to the ribbons settled on the Kapton film.

The techniques presented by Qi et al. and Park et al. have two key points that allow the films to be transferred. One is the etching process that separates the ceramic ribbons and the mother substrate, and the other is the use of PDMS stamps for lifting the ribbons. It should be noted that the etching for the film/substrate separation is possible only when the films are in the shape of ribbons with exposed mother substrate surface in between. In our process, on the other hand, it is the release layer that allows the film/substrate separation, and hence even large area thin films can be lifted off without any etching process. As the use of PDMS is concerned, in our process the adhesion of ceramic thin films to plastic substrates is realized by melting or softening of the plastic substrate surface, which makes the lift-off process applicable to any kinds of plastic substrates. Thus our process is much more advantageous in that ceramic thin films on plastics can be realized regardless of the coating area and irrespective of the combination of plastics and ceramics. In addition, the whole process can be conducted in the ambient atmosphere, which provides a great advantage for industrial production. Thus the technique proposed here may reform the concept and possibility of the techniques for depositing ceramic thin films on plastics that may be used as functional materials and devices in a variety of application fields.

## CONCLUSIONS

A new technique for fabricating ceramic thin films on plastics has been proposed, where (i) a polymer release layer is deposited on a silicon substrate, (ii) a precursor gel film is deposited on the release layer by spin- or dip-coating, (iii) the gel film is fired into a ceramic film, and (iv) the fired ceramic film is transferred onto a plastic substrate by melting or softening the substrate surface. The ceramic thin films transferred onto plastic substrates were crack-free and had smooth surface. Transparent, 60 nm thick anatase thin films with high optical reflectivity could be prepared on PMMA and PC substrates, and transparent, 660 nm thick ITO thin films with electrical conductivity were realized on PC substrates. Patterned ITO thin films on plastics could also be fabricated by using a mother silicon substrate with periodic grooves. The

technique is significant in that the crystallization and densification, which are key factors for superior functionalities, are guaranteed for the films by the firing process, and that the principle of the technique allows any kinds of ceramic thin films to be fabricated on any kinds of plastic substrates.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Surface roughness profiles of the release layers and ceramic thin films (Figure S1), IR absorption spectra of the release layers (Figure S2), XRD patterns of the TiO<sub>2</sub> thin films (Figure S3), and optical absorption and reflection spectra of the ITO thin films (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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