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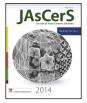
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Fabrication of highly crystalline oxide thin films on plastics: Sol–gel transfer technique involving high temperature process

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A B S T R A C T

Si(100) substrates were coated with a polyimide (PI)–polyvinylpyrrolidone (PVP) mixture film, and an alkoxide-derived TiO_2 gel film was deposited on it by spin-coating. The gel films were fired under various conditions with final annealing at 600–1000 °C. The PI–PVP layer was completely decomposed at such high temperatures while the TiO_2 films survived on Si(100) substrates without any damages. When the final annealing temperature was raised, the crystalline phase changed from anatase to rutile, and the crystallite size and the refractive index of the films tended to increase. The TiO_2 films thus fired on Si(100) substrates were transferred to polycarbonate (PC) substrates by melting the surface of the plastic substrate either in a near-infrared image furnace or on a hot plate under a load. Cycles of deposition and firing were found to be effective in achieving successful transfer even for the films finally annealed at 1000 °C. X-ray photoelectron spectroscopic analyses on the film/Si(100) interface suggested that the residual carbon or carbides at the interface could be a possible factor, but not a necessary and decisive factor that allows the film transfer.

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1. Introduction

Crystalline oxide thin films deposited on plastic substrates have a number of applications in the field of flexible electronic devices including flat-panel displays, large area radio-frequency communication devices, structural health monitors, conformal X-ray imagers, and flexible solar cells [1,2]. Their applications may spread over a wider field, considering the variety of the functionalities of oxide crystals based on their optical, electrical, magnetic, dielectric, and chemical properties.

So far great efforts have been made on "low-temperature processing" as reviewed in Ref. [3] where thin films are crystallized without firing so that plastic substrates can survive. Higher crystallinity, i.e. larger volume fraction of crystals and larger crystallite size, is achieved, however, by activated atomic diffusion via firing, which in many cases brings about better performances of oxide thin films. Aiming at providing highly crystalline oxide films on plastic substrates, we have recently developed a new technique

which is based on sol–gel thin film deposition and transfer [3–6]. The technique comprises (i) the deposition of a polyimide (PI) or PI-polyvinylpyrrolidone (PVP) mixture film on a silicon substrate, (ii) the deposition of a precursor gel film on the polymer film, (iii) the firing of the gel film, and (iv) the transfer of the fired oxide film onto a plastic substrate. The firing process guarantees the crystallization of the oxide film, and the PI or PI–PVP film acts as a release layer that aids the oxide film to be delaminated from the silicon substrate. The transfer is achieved by melting the surface of the plastic substrate either in a near-infrared (IR) image furnace or on a hot plate under a load, where the molten plastics layer acts as an adhesive.

The firing and transfer processes were also employed by other groups, who fabricated crystalline oxide ribbons on polydimethylsiloxane rubbers [7–9]. They prepared oxide ribbons on a thermally resistant mother substrate by sputtering followed by firing, and etched the mother substrate through the intervals of the ribbons so that the ribbons can be detached from the mother substrate. Compared with their techniques our technique is superior; in that it even allows large area films to be fabricated on plastic substrates because it needs no etching process and utilizes release layers instead.

We believed that the release layer should not be completely decomposed in the firing process so that it aids the fired oxide

film to be detached from the silicon substrate on transfer. In other words, we believed that the firing temperature has an upper limit so that the release layer may survive. However, very recently we have noticed that the oxide film can be delaminated and transferred to a plastic substrate even when the release layer is completely decomposed by firing at high temperatures. Such a high temperature process may open a door to the realization of more highly crystalline oxide thin films on plastics.

In the present study, an alkoxide-derived TiO_2 gel film was prepared on a PI–PVP release layer on an Si(100) substrate, followed by firing at 600–1000 °C and transferring to a polycarbonate (PC) substrate in order to demonstrate the availability of the technique that involves the high temperature firing process. In order to clarify the factors that allow transfer, the effects of processing parameters on transfer were studied, wherein the parameters include the firing temperature, the number of cycles of thin film deposition, the thickness of plastic substrates and the method of transfer. Depth profiles of elements were also obtained by X-ray photoelectron spectroscopy (XPS) in order to examine the chemical species at the TiO_2-film/Si(100)-substrate interface. The effects of the firing temperature on the crystallinity, optical properties and porosity of the films were also studied.

2. Experimental

2.1. Preparation

N-methyl-2-pyrrolidone solution of polyamic acid (20 mass%, U-Varnish-S, Ube Industries, Ube, Japan), PVP (PVP K15, 10,000 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 release layers. A solution of mass ratios, U-Varnish-S:PVP:1-methyl-2-pyrrolidone = 6:1:2, was prepared by adding 1-methyl-2-pyrrolidone and PVP to U-Varnish-S, and the spin-coating was conducted on Si(100) substrates ($20 \times 40 \times 0.5$ mm^3) at a spinning rate of 8000 rpm, followed by heating up to 120 °C at a rate of 10 °C min^{-1} 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^{-1} between different temperatures. Finally ca. 1.4 μm-thick PI–PVP mixture layers with smooth surface were obtained on Si(100) substrates.

A solution of mole ratios, $Ti(OC_3H_7{}^i)_4$:H_2O:HNO_3:C_2H_5OH = 1:1: 0.2:20, was prepared in the following manner using $Ti(OC_3H_7{}^i)_4$, nitric acid (69–70%) and ethanol, all purchased from Wako Pure Chemical Industries, and ion-exchanged water as the starting materials. A solution consisting of water, nitric acid and a half of the prescribed amount of ethanol was added to a solution comprising $Ti(OC_3H_7{}^i)_4$ and the other half amount of ethanol under magnetic stirring. The homogeneous, transparent solution thus obtained was kept at room temperature for 30 min, and served as the coating solution. The TiO_2 gel film was prepared on the release layer by spin-coating at 8000 rpm, followed by exposure to water vapor for 1 h. After the exposure, the gel film was heated up to 600–1000 °C at 5 °C min^{-1} in an electric furnace. In some cases the gel film deposition and the firing at 600 °C were cycled up to five times, followed by the final annealing at 600–1000 °C for 10 min, where the first gel layer was heated up to 600 °C at 5 °C min^{-1} and the second to fifth gel layers were heated by placing them in an electric furnace of 600 °C for 10 min. The thickness of a fired single-layer TiO_2 film was ca. 60 nm, and the release layer was completely decomposed during the heat treatment as shown in Section 3.

The fired TiO_2 thin films were transferred onto PC substrates ($20 \times 20 \times 5$ mm^3 or of $20 \times 40 \times 1$ mm^3) either in a near-infrared (IR) image furnace or on a hot plate with a roller with the

sample configurations shown in Fig. 1. In the case of the former, a PC($20 \times 20 \times 5$ mm^3)/TiO_2-film/Si(100) stack that was bound with binder double clips (Fig. 1(a)) was heated up to 170 °C at 75 °C min^{-1} in a near-IR image furnace (MILA3000-P-N, ULVAC-RIKO, Kanagawa, Japan), where the Si(100) substrate absorbs the near-IR light and radiates the heat. The 5 mm thick PC substrate instead of the 1 mm thick one was used so that unidirectional pressure high enough for the transfer is realized by the binder double clips. In the case of the latter, the TiO_2 film on the Si(100) substrate was placed on a hot plate of 180 or 190 °C with the Si(100) rear side being contacted with the hot plate. Then a PC substrate ($20 \times 40 \times 1$ mm^3) was pressed on the TiO_2 film by a stainless roller (20 cm in diameter, 2.4 cm in width and 6.44 kg in weight) that was rotated very slowly so that the center of the roller moves horizontally at a rate of 2.44 mm min^{-1} (Fig. 1(b)). The 1 mm thick PC substrate, which was flexible and bendable, was used instead of the 5 mm thick one so that the air between the PC substrate and the TiO_2 film on Si(100) is squeezed out and the effective contact is realized between them.

2.2. Measurements and observations

The thermal decomposition behavior was studied on the release layer by thermogravimetric and differential thermal analyses (TG–DTA) conducted at a heating rate of 5 °C min^{-1} in flowing air using a thermal analyzer (TG8120, Rigaku, Tokyo, Japan). The release layer on the Si(100) substrate was scraped off with a surgical knife and served for the analysis. The thermal decomposition of the release layers was also traced by measuring the IR absorption spectra on the film samples on Si(100) substrates using a Fourier transform IR spectrophotometer (FT/IR-410, JASCO, Tokyo, Japan) where a bare Si(100) substrate was used as the reference.

The "transferred area fraction", i.e. the fraction of the area of the film that was successfully transferred to the PC substrate, was obtained by image analysis using GIMP 2 (GNU Image Manipulation Program 2). Whether or not the TiO_2 film had cracks was examined by an optical microscope (KH-1300, HiROX, Tokyo, Japan). The crystalline phases of the TiO_2 films were identified with an X-ray diffractometer (Rint 2550 V, Rigaku, Tokyo, Japan) with Cu Kα radiation operated at 40 kV and 300 mA. The crystallized size was obtained from the corrected half-height width of the diffraction peak using Scherrer's equation. The optical absorption spectra were measured on the samples on PC substrates using an optical spectrometer (V-570, JASCO, Tokyo, Japan), where the reference was the air. The reflection spectra were recorded using the same spectrometer with a reflection attachment (SLM-468, JASCO). The refractive index and the thickness of the films were measured on the films on Si(100) substrates with a single-wavelength ellipsometer (ESM-1T, ULVAC, Chigasaki, Japan) with a He–Ne laser at an incident angle 70° and a spectroscopic ellipsometer (M-2000V-Kk, J.A. Woollam Company, Nebraska, USA) at three angles of incidence of 65°, 70°, and 75° over the spectral range 370–1000 nm. The porosity p was calculated from the refractive index n_f by the following equation [10]:

$$1 - p = \frac{(n_f^2 - 1)(n_c^2 + 2)}{(n_f^2 + 2)(n_c^2 - 1)} \tag{1}$$

where n_c is the refractive index of anatase or rutile.

The chemical compositions and their depth profiles were obtained for the films on the Si(100) substrates using an X-ray photoelectron spectrometer (PHI5000 Versa Probe, ULVAC-PHI, Chigasaki, Japan) with a monochromatic Al Kα X-ray source. To counter the surface charging, a charge neutralizer was used during the collection of the spectra. The depth profiling of the compositions was obtained by collecting the spectra after every 60 s sputtering by Ar$^+$ ions.