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On-site fabrication of ceramics films from solution precursors by ink-jet and spray assisted processes

Atsushi Matsuo · Ruwan Gallage · Takeshi Fujiwara · Tomoaki Watanabe · Masahiro Yoshimura

Abstract Solution processing based on Ink-jet and spray technologies is one of low cost on-site ceramic patterns/films fabrication methods at moderate temperatures from precursor solutions. In the present study, we have used ink-jet and spray technologies to fabricate ceramic films of titania directly on glass substrates at 300–400°C. The precursor solution was prepared by dissolving Titanium tetraisopropoxide in appropriate solvents (water/ethanol and acetylacetone). A cleaned glass substrate was kept on a hot plate and heated it up to a predetermined temperature. Droplets of the precursor solution produced through a spray gun were traveled towards heated substrate with a atmospheric pressure. When the droplets hit on the heated substrate, precursor started to decompose, nucleate and grow into the TiO_2 film. The anatase pattern was directly obtained by ink-jet method at moderate temperatures.

Keywords Titania · Anatase · Pattern · Film · Solution

1 Introduction

Solution processing [1] for ceramic film/pattern can be defined as an environmentally friendly processing technique using aqueous solutions. It may also provide similar results by the other processes that use higher energetical precursor like vapor, gas and plasma with/without vacuum systems.

A. Matsuo (✉) · R. Gallage · T. Fujiwara · T. Watanabe · M. Yoshimura
Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, Japan 226-8503
email matsushi@msl.titech.ac.jp

Solution processing based on Ink-jet [2] or spray technologies [3] is a low cost on-site fabrication method for ceramic pattern and film [4] at moderate temperatures using aqueous precursor solutions [5]. In the present study, we have used ink-jet and spray technologies to fabricate ceramic films of TiO_2 at moderate temperatures.

2 Experimental

2.1 Preparation of titania precursor solution

Titanium tetraisopropoxide was dissolved in a mixture ethanol, nitric acid and distilled water. The molar ratio of titanium, ethanol, nitric acid (66 wt%) and distilled water is 1: 20:1.5:1. This solution was dried using a hot-plate at 40°C for 12 h. After the solvent evaporated, the obtained powders were dissolved in the mixture of distilled water and Ethanol (Volume ratio was 80/20). Then few microliter of hydrogen peroxide solution (31 wt%) and Acetylacetone (AcAc) were added into this aqueous solution. AcAc can act as a chelating agent and molar ratio of AcAc:Ti was 1.25:1. The final yellow precursor solution was 0.02M and can be kept to for several months without any change like precipitation. This solution was used for fabricating titania patterns/films at elevated temperatures using ink-jet and spray technologies.

2.2 Fabrication of titania films and patterns

Cleaned glass substrates (Corning Inc., #7059) was kept on the hot-plate and heated up to a predetermined temperature. Droplets of the precursor solution were produced through a spray gun (Fig. 1) or by the nozzles of ink-jet head (microFab Tech. Inc., MJ-AB-01-30) (Fig. 2) towards the heated substrate under an atmospheric pressure. When the droplets

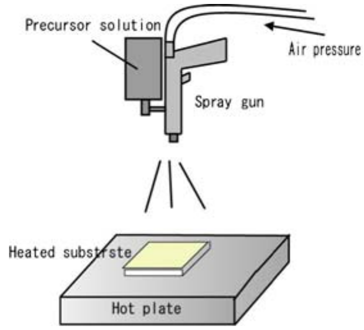

Fig. 1 Spray method

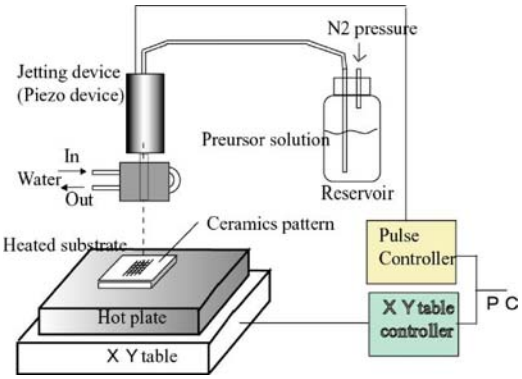

Fig. 2 Ink-jet method

reach the heated substrate, the precursor begins to decompose, nucleate and then grow thus ceramic materials form a film. A TiO_2 film was fabricated by spraying the precursor solution for 45 s and waiting for 4 s till the substrate temperature return to the prefixed value. This process was repeated for 15 times. Some of the deposited films were heated unto ~600°C by a burner flame.

The obtained products were characterized by X-ray diffraction (XRD) (MXPS^{3VA}, Mac Science Co. Ltd., Japan), using Cu Kα radiation. The surface morphology was observed by Laser Microscopy (LSCM) (VK8510, Keyence, Japan) and Scanning Electron Microscopy (SEM)(S4000, Hitachi, Japan). Visible Raman spectra were collected using a Jobin/Atago Bussan T64000 Triple spectrometer equipped with a 514.5-nm visible laser.

3 Results and discussion

Figure 3 shows X-ray diffraction patterns (XRD) for the fabricated thin films on the glass substrate by the spray deposition method at different temperatures at 300, 350 and 400°C. Comparing the peak position with the data from JCPDS, it can be seen that, the deposited film on the substrate has crystallized into anatase phase even at 300°C.

Figure 4 shows the Raman spectra for TiO_2 films prepared by the spray deposition at different temperatures and

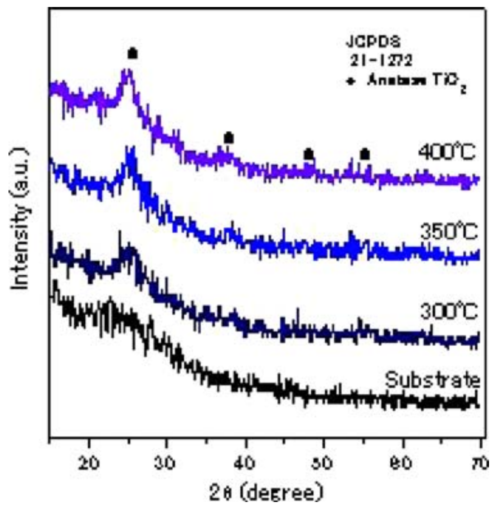

Fig. 3 XRD patterns for the films fabricated at different substrate temperatures by spray deposition

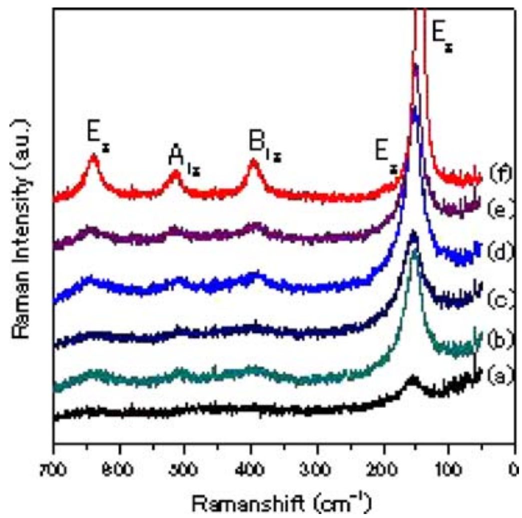

Fig. 4 Raman spectra for (a) as deposited, (b) the pattern prepared by ink-jet at 275°C, (c) the film prepared by spray at 300°C, (d) 350°C, (e) 400°C and (f) the film prepared at 400°C after heat-treatment ~600°C with the burner

by the ink-jet at 275°C respectively. Five raman modes are attributed to the anatase phase with the symmetries of E_g, E_g, B_{1g}, A_{1g}, and E_g. The peak of the E_g mode around 151 cm^{-1} shifted towards higher wavenumbers and had more broadened width than that of the bulk. It might indicate that small crystal size and the existence of oxygen defects because of low temperature as reported previously [6, 7]. In fact, the Raman peak around 143 cm^{-1} moved back to the position around 150 cm^{-1} of the bulk anatase crystal after heat-treatment (~600°C) by a burner flame, as seen in Fig. 4f. It means the crystallinity of the anatase phase could be increased by the heat-treatment. According to the XRD and Ramen data, we can conclude that crystallized anatase films could be fabricated at ~300°C on glass substrates.

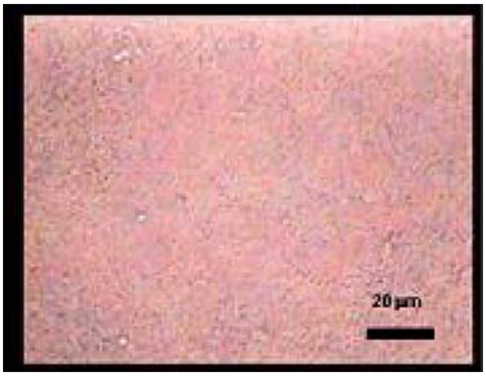

Fig. 5 Laser microscopic image of TiO_2 film prepared on glass substrate by spraying at 350°C

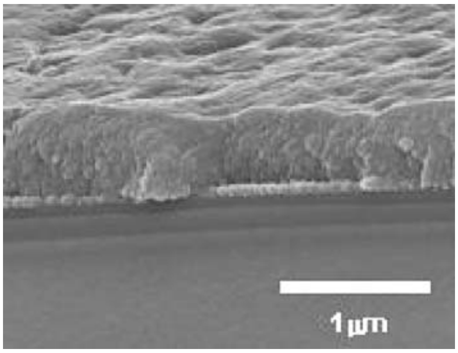

Fig. 6 Cross sectional SEM image of TiO_2 film prepared on glass substrate by spraying at 350°C

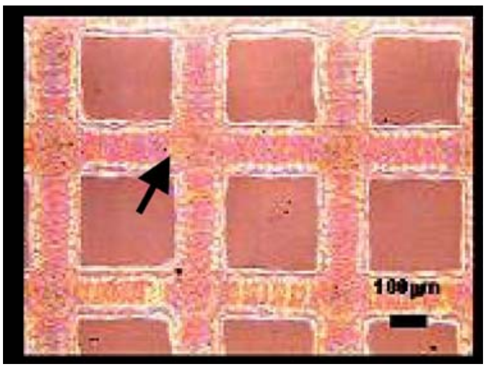

Fig. 7 Laser microscopic images of TiO_2 pattern prepared on glass substrate by ink-jetting at 275°C

Figure 5 shows Laser microscopic image of the film surface prepared at 350°C. It has no cracks nor significant inhomogeneities like droplet marks. The adhesion of the films was also good without any peeling and crack.

Figure 6 shows the SEM image for the cross-section of the film prepared at 350°C. The film had about 700 nm thickness after 15 times spraying composed of about 20 nm particles size. It can be observed that particles deposited layer by layer in random orientation.

Figure 7 shows the TiO_2 pattern made by the ink-jet technology on the substrate at 275°C. This net shaped pattern was

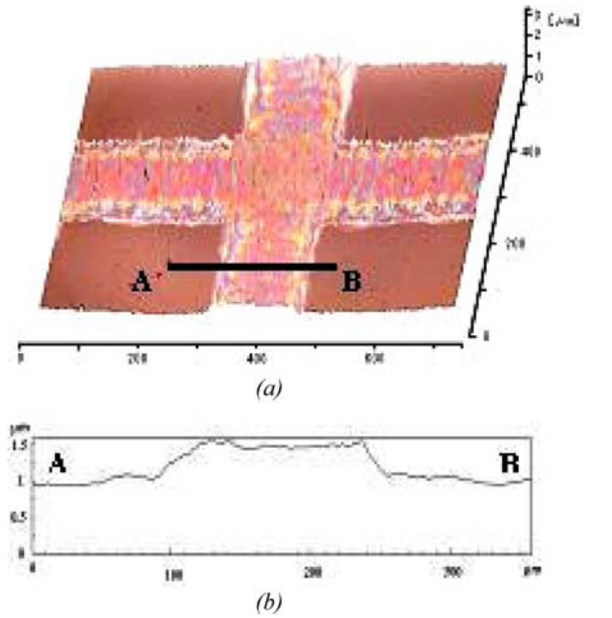

Fig. 8 (*a*) 3-D. Laser microscopic image of the pattern and (*b*) the height distribution along AB line

fabricated directly from the same solution as that for spraying. The pattern had the line width of about 120 μm and a relatively smooth surface with about 420 nm in height after 10 shots of droplets and 30 μm dot-pitch by using 30 μm nozzle diameter as seen in Fig. 8, however it may become much narrower and lower if much smaller ink-jet head can be used [8].

4 Conclusions

TiO_2 thin films were prepared by the spray deposition from the precursor solution. Films sprayed at substrate temperature above 300°C were crystallized into anatase phase. Those films had free of cracks and the thickness about 700 nm. TiO_2 patterns were made directly by ink-jetting deposition on glass substrate at 275°C with the same solution. They had about 120 μm width and about 420 nm height. The anatase deposited at those moderate temperatures had broadened and higher wave-number shifted E_g raman peak probably due to smaller crystallite size and/or some defects. This ink-jet processing is the direct fabrication process from the precursor solution without any masking and etching processes. Therefore this route may serve as an inexpensive and environmentally friendly technique for the fabrication of patterned films.

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