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Titanium oxide film deposition by vortex air thermal plasma assisted spray pyrolysis deposition†

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KEY WORDS: (Titanium oxide) (Photo-catalysis) (Thermal plasma) (Thermal spray) (CVD) (Dye sensitized solar cell)

1. Introduction

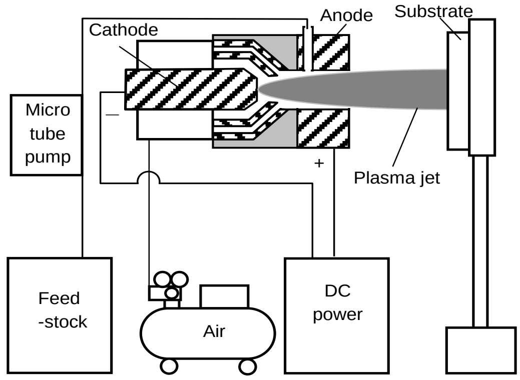
Spray pyrolysis deposition (SPD) is a rapid film deposition process. Various functional material films, such as SnO_2 [1], YSZ [2], $CuInSe_2$ [3] and so on, have been successfully deposited so far. Especially, in the case of oxide film deposition, film deposition can be carried out in open air. Therefore, SPD is hoped to be a low cost deposition process for functional material films. However, since film was deposited by chemical reaction of non-activated precursors on the substrate, substrate should be heated over 773 K in the case of conventional SPD. So, it was very difficult to apply this process to low melting point materials such as plastics.

In this study, in order to develop a low temperature film deposition process using spray pyrolysis deposition, as a basic study, titanium oxide film deposition by vortex air thermal plasma assisted spray pyrolysis deposition was carried out.

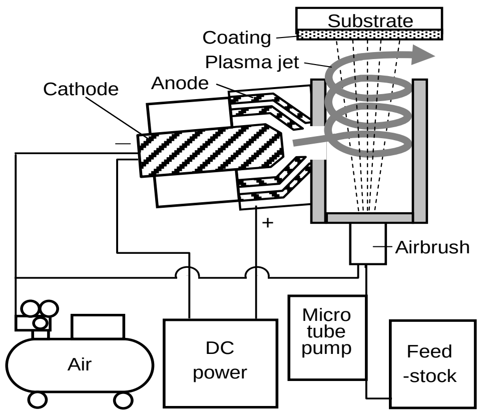
2. Experimental Procedure

In this study, two types of SPD equipments, which were straight plasma jet assisted SPD equipment and vortex plasma jet assisted SPD equipment, were used. These SPD equipments consisted of plasma torch, DC power supplying system, micro tube pump (feedstock supplying system) and working gas supplying system as shown in **Fig. 1**. **Table 1** shows deposition conditions. The plasma torch has water cooled electrodes. The anode is made from copper, has feedstock feeding port at the head and has a constrictor which is 6 mm in diameter. A cylindrical cathode made from tungsten has a diameter of 5 mm. Air was used as working gas. Mass flow rate of the gas was fixed at 50 l/min. As the feedstock for titanium oxide film deposition, ethanol diluted titanium tetra iso butoxide ($Ti(OC_4H_9)_4$) was used. Substrates were 15mm x 15mm x 1mmt 304 stainless steel plates with #400 sand paper polished surface. The spray distance (the distance between the nozzle outlet of the plasma torch and the surface of the substrate) was fixed at 100 mm. The deposition time was 7 min. The discharge power was 10A/ 100V. In the case of vortex plasma jet assisted SPD equipment, a commercial airbrush was used as feedstock spraying equipment.

After titanium oxide films deposition, investigations were made of the microstructure of the film by X-ray diffraction (CuKα, 40 kV, 100 mA). Besides, in order to confirm photo-catalytic property of the film, methylene-blue droplet test and its decoloration test using UV irradiation equipment (**Fig. 2**) were carried out.



a) Straight plasma jet type



b) Vortex plasma jet type

Fig. 1 Schematic diagrams of the SPD equipments.

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Table 1. Film deposition conditions .

Air working gas flow rate	50 l/min.
Discharge Power	10A/ 100V
Deposition distance	100 mm
Deposition time	7 min
Feedstock	C_2H_5OH diluted TTIB* solution
Feedstock feed rate	200 ml /h
Subatrate	304 stainless steel

*TTIB: Titanium tetra iso butoxide

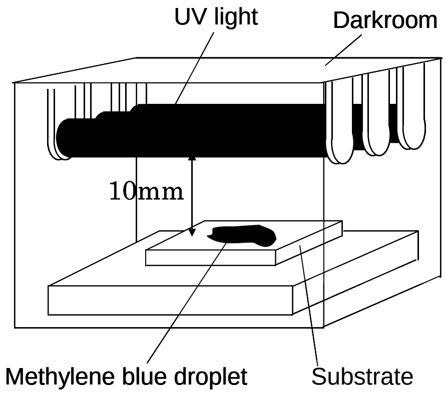


Fig. 2 Equipment for methylene-blue decoloration test.

3. Results and Discussion

Film deposition by straight plasma jet assisted SPD

Since thermal plasma has steep axial and radial profiles, deposition distance is one of the most important operation conditions affecting the film structure and component. **Figure 3** and **4** show the appearance and XRD pattern of the sample deposited on the condition of 100mm in deposition distance. The deposition temperature was approximately 673 K. As for the appearance of the sample, gray color film with coarse surface was deposited. As the reason why the film became coarse, it was thought that the partially vaporized and activated feedstock was fed to the substrate surface because the feedstock was fed to the plasma jet as droplets due to its surface tension of the feedstock. However, in the XRD pattern, diffraction peaks indicate TiO_2. Especially, anatase which is known as excellent photo catalytic material was dominant in the deposited titanium oxide film. As photo-catalytic property detection methods, wettability testing and methylene-blue decoloration testing are relatively easy methods. **Figure 5** shows appearances of the sample before and after methylene-blue decoloration test. The films were hydrophilic and it was observed that the methylene-blue droplet was slightly decolored after only 4 hour UV irradiation.

Film deposition by vortex plasma jet assisted SPD

In the case of vortex plasma jet assisted SPD, since the substrate could not be heated by plasma jet directly, the substrate temperature during deposition was under 623 K on the condition of 100 mm in deposition distance. Therefore, amorphous titanium oxide film was deposited. However, by post heat (723 K, 30 min.), the amorphous film could be changed into anatase dominant film. Besides, it was confirmed that the anatase film has photo catalytic properties according to the methylene-blue decoloration test.

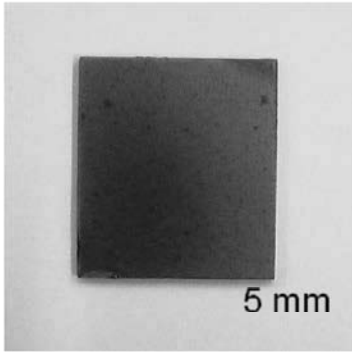


Fig. 3 Appearance of the TiO_2 film deposited substrate.

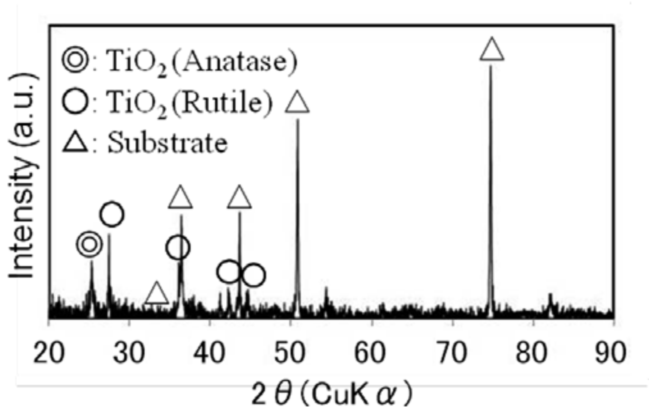
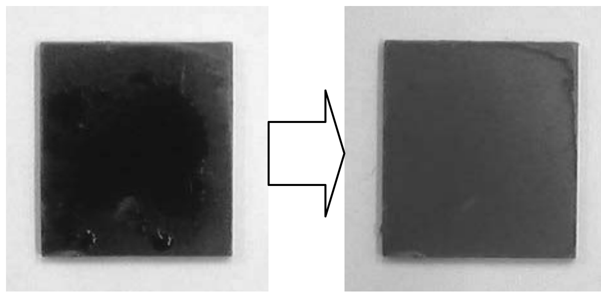


Fig. 4 XRD pattern of the TiO_2 film deposited substrate.



a) 0 hr b) 4 hr

Fig. 5 Results of metylene blue decoloration testing in the case of TiO_2 film deposited substrate

4. Conclusions

In order to develop a high rate and low cost functional oxide film deposition process, deposition of titanium oxide film by two types of SPDs using air working gas was carried out. Consequently, anatase dominant gray color film could be obtained and it was confirmed that the anatase films had photo-catalytic properties by the methylene-blue droplet test and its decoloration test. From these results, this technique was found to have high potential for high rate and low cost functional oxide film deposition.

References

[1] T. Nagamoto, M. Endo, O. Omoto: Jpn. J. Appl. Phys. 18, 6 (1979), pp.1103-1109.
[2] H. Ishizawa: Am. Ceram. Soc. Bull. 65 (1986), pp.1399-1402.
[3] S. Shirakata, H. Kubo, C. Hamaguchi, S. Isomura: Jpn. J. Appl. Phys. Pt. 2, Letters 36, 10B (1997), L1394-L1396.