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TiO_2 thin film coating on a capillary inner surface using atmospheric-pressure microplasma

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ABSTRACT

Titanium dioxide (TiO_2) thin films were prepared on a capillary inner surface on a glass chip using plasma-enhanced chemical vapor deposition (PE-CVD) with titanium tetraisopropoxide and oxygen as reactants and helium as the carrier gas at atmospheric pressure. A microplasma was generated inside the capillary with a cross section of 1×1 mm^2 and a length of 15 mm by radio frequency excitation of 13.56 MHz using externally attached parallel-plate electrodes. After 60 min deposition, transparent thin films were deposited on a capillary inner surface. X-ray photoelectron spectroscopy revealed that the deposited films are in the chemical binding state of TiO_2. Scanning electron microscopy images showed that TiO_2 thin films have somewhat rough surface with micro/nanoparticles. Typical film thickness was approximately 200 nm. Spatial distribution of the film thickness was also measured by 3 dimensional surface structure analyzer.

1. Introduction

Surface modification of microfluidic channel walls for controlling surface chemistry and zeta potential are of considerable interest in fabrication of micro-capillary electrophoresis (CE) chips for analysis of proteins and DNA. Several studies on plasma treatment of the inner wall of microfluidic channel on a chip have been reported, including chemical surface modification of polymer microfluidic devices for the zeta-potential control [1–3] and plasma-enhanced chemical vapor deposition (PE-CVD) of platinum thin films on a microchannel fabricated in a Pyrex glass chip [4]. Atmospheric-pressure microplasmas (APμPs) are very useful for inner surface modification in a capillary on a sealed microfluidic device, since the reactive plasma can be generated inside the capillary without using a vacuum chamber. Furthermore, the atmospheric plasma provides higher plasma density than a vacuum plasma and non-thermal plasma is obtained due to the large surface/volume ratio and low-discharge current of the microplasma. However, there are few studies that tried to investigate PE-CVD on the inner surface of a sealed microchannel using the APμP.

In this study, titanium dioxide (TiO_2) thin films were prepared on a capillary inner surface of a sealed glass chip by APμP using titanium tetraisopropoxide (TTIP) and oxygen (O_2) as reactants and helium (He) as the carrier gas. TiO_2 thin films are widely used as photocatalysts [5]. For example, some applications of a TiO_2-coated capillary are zeta-potential control of the microfluidic devices due to the highly hydrophilic property of TiO_2 surface under UV light irradiation and microreactor chips such as the oxidation of organic compounds including antibacterial effect. APμP was generated inside a capillary by radio frequency excitation using externally attached parallel-plate electrodes. The performance of PE-CVD of TiO_2 films on a capillary inner surface by APμP is examined by studying the surface morphologies, chemical binding states and 3-dimensional surface profiles of the deposited films.

2. Experimental

TiO_2 thin films were prepared on the inner surface of a sealed glass chip by PE-CVD using TTIP as the precursor at atmospheric pressure. The experimental apparatus used in this study is schematically shown in Fig. 1. The glass chip was fabricated by putting two pieces of slide glasses and a pair of spacing glasses with a thickness of 1 mm together. The chip size was $38 \times 26 \times 3$ mm^3. The cross section and a length of a capillary were 1×1 mm^2 and 28 mm, respectively. The parallel-plate copper electrodes of 1.0 mm in width and 15 mm in length were externally attached onto the glass chip so that the capillary might be sandwiched between the two electrodes. One electrode was connected to an RF generator (frequency of 13.56 MHz) via a miniaturized matching circuit [6], while the other was grounded. Flow-controlled gases were introduced into the capillary and drawn off to the air, and therefore, the plasma was generated at atmospheric pressure. The excitation mechanism of the APμP is similar to that of atmospheric-pressure glow discharge, i.e., dielectric barrier discharge [7,8]. TTIP liquid was stored in a small glass bubbler (6 mL) and maintained at 45 °C using a heating tape. The TTIP vapor was carried by He (99.9999% purity) at a flow rate of 490 sccm. The TTIP vapor and O_2 (99.99% purity) were mixed before being introduced into the capillary. The gas line of the TTIP vapor was heated to 45 °C to prevent condensation of vapor during transfer.

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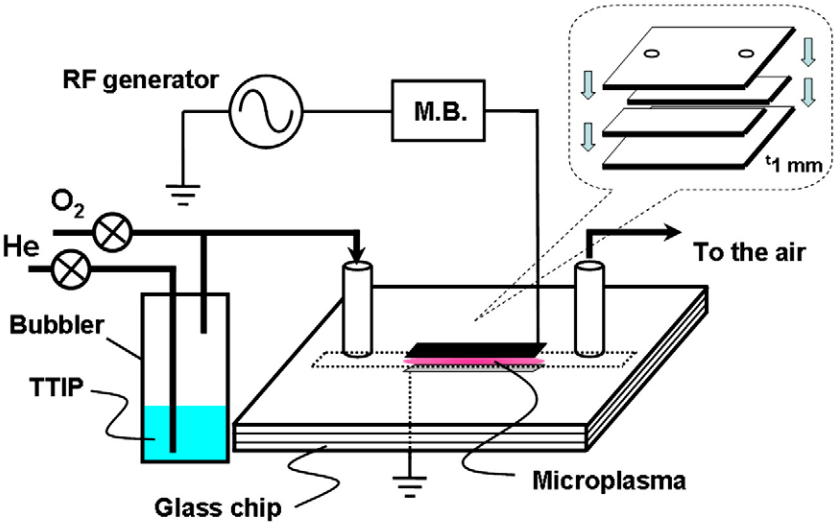

Fig. 1. Schematic diagram of experimental setup for TiO_2 thin film coating on a capillary inner surface of a sealed glass chip.

The deposition conditions of the TiO_2 thin films are as follows. The total gas flow rate was 500 sccm, the O_2 flow rate was 10 sccm, RF power was 12 W and the deposition time was 60 min. The glass chip as a substrate was not externally heated but was self-heated by the plasma irradiation. The outer-surface temperature of the glass chip measured by a thermocouple was approximately 140 °C. The surface morphology of the deposited film was examined by scanning electron microscopy (SEM, JSM-5800LV) and the surface distribution of elements was also characterized using an energy dispersive X-ray (EDX, JED-2110) analysis. The chemical binding state of the thin films was analyzed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI ESCA 5600 Ci). The spatial distribution of the film thickness was measured by 3-dimensional imaging surface structure analyzer (Zygo, New View 200).

3. Results and discussion

Photograph of the APμP generated in a capillary on a sealed glass chip is shown in Fig. 2. Discharge gas is a pure He. The gas flow rate and RF power are 500 sccm and 10 W, respectively. It can be seen that plasma was generated just under the excitation plate electrodes.

After 60 min deposition, transparent thin films were prepared on a capillary inner surface. To examine the surface morphology of the deposited films and their chemical composition, SEM and EDX were utilized. The EDX images of Si, O and Ti elements in the channel area on a glass plate as well as the corresponding SEM image are shown in Fig. 3. Ti element was detected over all area. However, there was light and shade on the Ti mapping and also Si element as a background spread over the whole area. It implies that the spatial distribution of TiO_2 films is not uniform and the average thickness of TiO_2 films was so thin (<1 μm) that X-ray penetrated the thin films to a glass substrate. Fig. 4 shows the SEM image of surface morphology of the deposited TiO_2 films. In Fig. 4, the area focused on the SEM observation is positioned in the right hand of the SEM image shown in Fig. 3. The SEM image showed that TiO_2 thin film has somewhat rough surface with micro/nanoparticles. TTIP, i.e., $Ti(O–i–C_3H_7)_4$, is decomposed by energetic ions and radicals generated by the plasma and intermediate products, such as $Ti(OH)(O–i–C_3H_7)_3$ and $Ti=O(O–i–C_3H_7)_2$ radicals react with each other on a substrate. Therefore, TiO_2 films were prepared on a substrate via nucleation and growth, i.e., Volmer–Weber type, mechanism [9]. On the other hand, it seems that these micro/nanoparticles were synthesized and grown in plasma gas phase due to the oxidation of the TTIP precursor because there are a great number of atomic oxygen radicals at atmospheric pressure.

The chemical binding states of Ti and O in the deposited films were studied by XPS measurements. XPS spectra of Ti 2p and O 1s from the surfaces of the deposited films are shown in Fig. 5. An electron flood gun was used to eliminate the surface charging during the XPS measurements. The Ti $2p_{3/2}$ peak and Ti $2p_{1/2}$ peak are located at 458.8 eV and 464.6 eV, respectively. These two peak positions correspond to the TiO_2 state [10]. For the O 1s spectrum, the double Gaussian fitting whose peak positions are located at 530.1 eV and 531.3 eV, respectively, reproduced the experimental result. The peak at 530.1 eV is due to the oxide component (530.1 ± 0.1 eV) in the TiO_2 [11–13]. On the other hand, the peak at 531.3 eV is originated from the oxygen in the hydroxyl groups OH or defective oxides (531.5 ± 0.5 eV) [13]. In fact, the peak position of the OH oxygen is usually recognized to be 1 to 1.5 eV higher than that of the oxide oxygen [14]. Therefore, it seems that the TiO_2 films deposited by APμP in this study contain hydrogen atoms. This result is just the same as that observed in the PE-CVD TiO_2 films [15].

Fig. 6 shows the 3-dimensional surface profile of TiO_2 films deposited on a glass plate. It can be seen that TiO_2 films were deposited under the electrodes but the spatial distribution of the film thickness was not uniform. The deposition volume of TiO_2 films gradually decreased from the center of the electrode to the gas outlet.

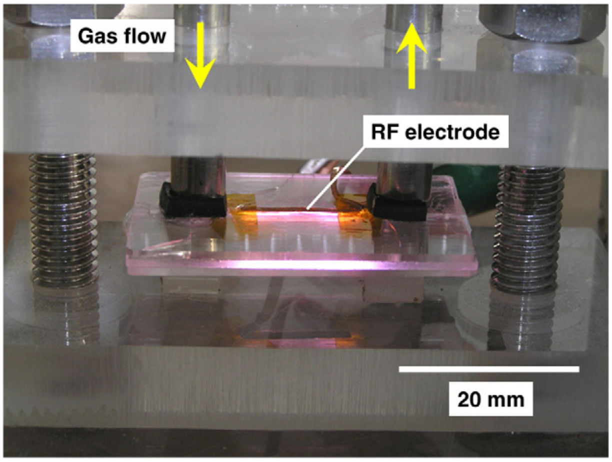

Fig. 2. Photograph of atmospheric-pressure He microplasma generated in a capillary on a chip.