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Laser ablated plasma plume characteristics for photocatalyst TiO_2 thin films preparation

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Abstract

The TiO_2 plasma plume produced by pulsed laser deposition (PLD) using a Nd:YAG laser (532 nm) is investigated by temporal and spatial resolved optical emission spectroscopy. Dynamics of neutral and ionized titanium species in the plume agreed with a drag model, which was explained as a collision between the excited species and ambient gas. The velocity of neutral oxygen atoms is constant in spite of increasing the delay time after the laser irradiation and the distance from the target. The crystallinity of TiO_2 films deposited in the ablation plasma of Ti and TiN target was higher than that of TiO_2 target.

Keywords: Laser ablation; Plasma plume dynamics; Titanium dioxide

1. Introduction

Titanium dioxide (TiO_2) has attracted much attention for its photocatalytic applications in the field of environmental sanitation. If ultraviolet light is irradiated in TiO_2, an electron–hole pair generated across the band gap of TiO_2 would cause oxidation and reduction at the film surface. Numerous studies have reported on preparation of TiO_2 thin films by magnetron sputtering [1,2], chemical vapor deposition (CVD) [3,4], plasma source ion implantation (PSII) [5], pulsed laser deposition (PLD) [6] and sol–gel [7] methods, and characterization of structural, optical and photocatalytic properties of deposited TiO_2 thin films. In previous research, we prepared TiO_2 thin films at various deposition parameters (ambient gas, substrate temperature, target materials, post-annealing) by using PLD technique and reported on the relationship between the deposition parameters and film properties such as crystalline structure, morphology, chemical composition and decolorization ability [8].

Recently, the development of photocatalysts shows a high activity under visible and/or solar light irradiation. Visible light photoactivity has been introduced to TiO_2 by doping of nitrogen or transition metals such as Cr and Pt. We have also attempted to synthesize nitrogen-doped $TiO_{2-x}N_x$ thin films using TiN target in a nitrogen/oxygen gas mixture by PLD [9]. In photocatalytic test using methylene blue solution, the deposited $TiO_{2-x}N_x$ thin film was energized by visible light irradiation as well as UV light irradiation. However, the correlation between the properties of the deposited films and the plasma characteristics has not been dealt with.

This paper deals with a detailed spectroscopic investigation of plasma plume produced during the film deposition in order to estimate the processing plasma state and prepare high quality TiO_2 or $TiO_{2-x}N_x$ thin films. The temporal and spatial distributions and the optical emission species of plasma plume at various states using target materials and ambient gases were observed through a spectrometer and an ICCD camera.

2. Experimental

The laser ablation of Ti with purity 99.99%, TiN with purity 99.9% and TiO_2 with purity 99.99% targets was carried out using a Nd:YAG laser (Continuum SureliteIII;

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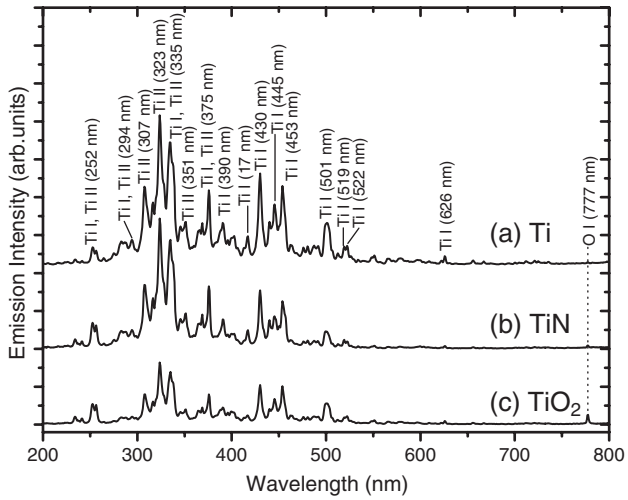

Fig. 1. Typical optical emission spectra of the plume produced by ablating Ti, TiN and TiO_2 targets at N_2+O_2 gas of 10 Pa.

wavelength of 532 nm, pulse duration of 3.5 ns, maximum output energy of 340 mJ), with a laser fluence of 4 J/cm^2 and a repetition rate of 10 Hz. The vacuum chamber was evacuated to a base pressure of 5×10^{-4} Pa by a turbomolecular pump, and then filled with O_2 gas or N_2 gas or a mixed (O_2+N_2) gas at a flow rate of 20 sccm.

The time- and spatial-resolved dynamics of the plasma plume created during the laser ablation process was analyzed through a spectrometer (Hamamatsu Photonics PMA-11) and an ICCD camera (Hamamatsu Photonics C5909-06), using a 20-ns fast gate pulse. The two-dimensional (2D) images of the plasma plume were observed as a function of a delay time (τ_d=100–5000 ns) after the laser irradiation. The optical emission spectra in the range of 200–800 nm were investigated at different delay times (τ_d=100–2000 ns) and different distances from the target surface (d=0.5–10 mm).

The film deposition silicon substrates were kept at 60 mm away from the target at a substrate temperature (Ts) of 400 °C. The structural property and chemical composition of the TiO_2 thin films deposited were characterized by using X-ray diffraction (XRD; RIGAKU RINT2100V) and X-ray photoelectron spectroscopy (XPS; JOEL JSP9010).

3. Results and discussion

The optical emission spectra of the plume produced by ablating Ti, TiN and TiO_2 targets in O_2+N_2 (O_2/

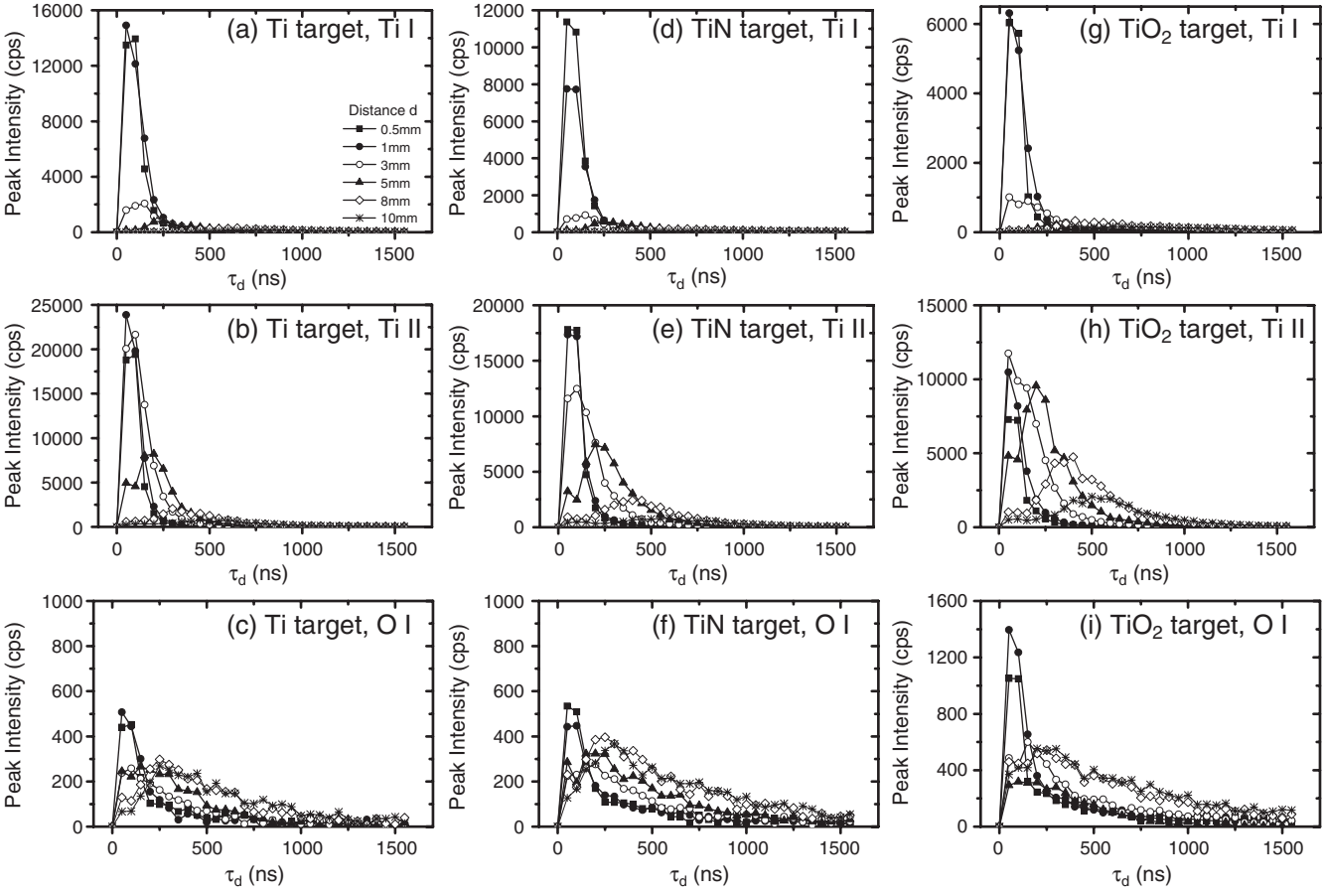

Fig. 2. Time (τ_d) dependence of the intensity of Ti I (430 nm), Ti II (323 nm) and O I (777 nm) emission peaks at different d from the target.