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Optical Spectroscopy of Plasma Plume Induced by Pulsed Laser Deposition of TiO_2 Thin Films

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The optical emission spectroscopy of the laser plasma plume during PLD in the growth of TiO_2 thin film is applied to the in-situ diagnostics. The peaks of the excited states of neutral atoms (Ti^* and O^*) and ion (Ti^{+*}) from the target (Ti or TiO_2) were assigned and explained the production process in qualitatively. The peaks from the excited states of the molecular (TiO^*) were observed and the production mechanism was explained by dependences of the buffer O_2 gas pressure in quantitative.
Key words: TiO, TiO_2, pulsed laser deposition (PLD), optical emission spectra, in-situ diagnostic

1. INTRODUCTION

Interest in pulsed laser deposition (PLD) as a technique to deposit thin films of complex materials is growing remarkably. Attempts to deposit a wide variety of materials have been spread widely. PLD have several advantages such as the variety for virtually any material, from pure elements to multicomponent compounds, reproduction for the stoichometry of the charge material in the film and the simple and economical system.

Optical emission spectroscopy is well suited as a diagnosis for yield information about laser plasma plume generated by PLD. The spectra of the plume are well reflected the density, temperature and contaminations of the plasma. For optical emission observation, the laser induced plume is an ideal as a bright plume extends several centimeters and viewed from the side by the naked eye. For the plenty of merits, it has been widely studied [1].

In the study of TiO_2, many efforts have been attempted to investigate the photocatalysis as its application to self-cleaning, anti-bacterial and air purifying materials [2]. For the preparing of TiO_2 thin films by PLD, the buffer oxygen gas is used for the oxidation [3]. The deposition is suitable for optical emission spectroscopy, since the buffer gas work like a test particle.

The optical emission spectroscopy is the most classical and elegant method in astronomical observations. In particular, the spectroscopy of titanium oxide (TiO) is very important to investigate the M-type star, such as Mira [4]. The studies of molecular line lists for the TiO molecule are prepared enough complete and accurate to be recommended for the construction of stellar atmosphere models [5, 6].

The application to the diagnostics and characteristics of laser-produced plasma of titanium are attempted [1]. The spectroscopy of 2 kW CO_2 laser welding of titanium [7] and of the pulsed laser in air at different ambient pressure [8] succeed to determined the temperature and other plasma parameters.

In this paper, the experiments of the optical emission spectroscopy in the growth of TiO_2 thin films and the observed effects of buffer dioxide gas are reported. The peaks in the spectra show existences of the excited states of Ti, O and TiO in the plasma. The production of the excited states is found to be originated in both the secondary mechanisms of the laser ablation and the collisions with the buffer oxygen gas.

2. EXPERIMENTAL

The experimental configuration was shown in figure 1.

The part of PLD system was similar to that used in the previous experiment [9]. The pulsed ArF Excimer laser was operating with wavelength 193 nm, pulse width 15 ns, repetition frequency 10 Hz and power 100 mJ. The laser beam was focused by a pair of cylindrical lenses onto a target with an incident angle of 45 degrees. The focal spot size was 1 x 2 mm, so the laser power density is evaluated to be 10^9 W cm^{-2}. The distance from the target to the substrate was about 5 cm. The target was a titanium Ti or a titanium dioxide TiO_2 disc that was continuous rotating during depositions. The substrates were α-Al_2O_3 single crystal with 10 x 10 mm were mirror polished at both sides and kept in room temperature during depositions. The growth chamber

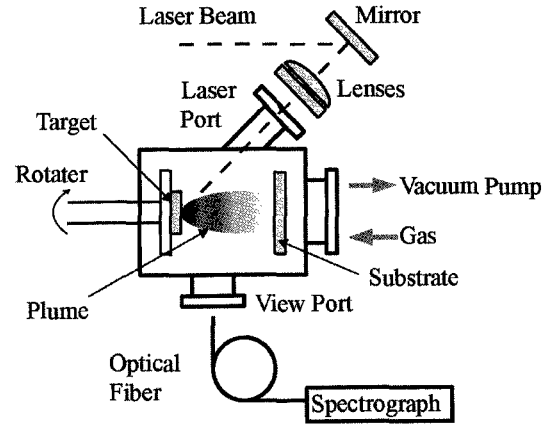

Figure 1. Experimental configuration for optical emission spectroscopy of PLD

was evacuated to a base pressure of about 3 x 10^{-5} Pa using a turbo molecular pump. Buffer oxygen gas was flowed into the growth chamber through a mass flowmeter to control the objected pressure.

Optical emission spectra from laser-produced plasmas plume were observed by a spectral measuring system through a view port. The material of the view port is fused silica with no surface coating, that the transmittance at the range under 240 nm is very low. The spectrometer consists the thermoelectric-cooling type Back-thinned (BT) charge coupled device (CCD) image sensors operated, which has quantum and a compact Czerny-Turner type spectrograph with F number 4, optical fibre probe and control circuit. The measurement wavelength region is 200 – 950 nm, and the resolution is about 2 nm (FWHM). All spectral intensities taken by the control computer system were also averaged over 100 cycles at the exposure time of 19 ms in each run.

3. RESULTS AND DISCUSSIONS

3.1 Optical spectra

The optical emission spectrum of the laser ablation plasma plume of titanium target in high vacuum (3 x 10^{-5} Pa) is shown in figure 2. Some peculiar lines of atoms oxygen [10,11] and titanium [10, 12] are assigned and denoted with the wavelengths and the Roman numeral notation. In the notation, the spectrum emitted by neutral atoms of a given element is called the first spectrum of that element, and is denoted by the Roman numeral I; the spectrum emitted by singly ionized atoms is called the second spectrum and is denoted by Roman numeral II; etc. Most of all peaks are not possible to describe into the fine structure, as the resolution of the spectrograph (< 2 nm) is larger than the separation (< 1 nm). For example, around 335 nm, there are Ti I [$1s^2 2s^2 2p^8 3s^2 3p^6$] $3d^2 4s^2$-$3d^2 4s4p$ (334.1875, 335.4634 nm), Ti II $3d^2 4s$-$3d^2 4p$ (334.904, 334.941 nm) and comparably week Ti III 3d4d-3d4f (335.4723 nm), but only "335 Ti I, II" was noted as main contribution. Except for Ti I and Ti II, there are some peak from O I in the range of larger than 770 nm. This oxygen is not originated from the buffer gas but from oxides on the surface of the target as described in 3.2.

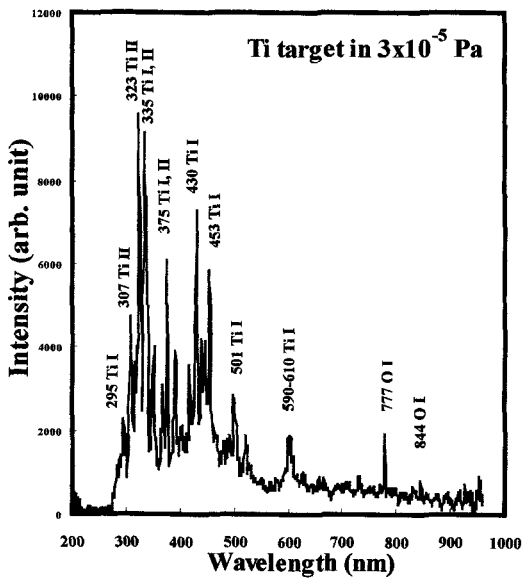

Figure 2. Optical emission spectrum of the laser ablation plasma plume from Ti target in 3 x 10^{-5} Pa ambient dioxide gas pressure

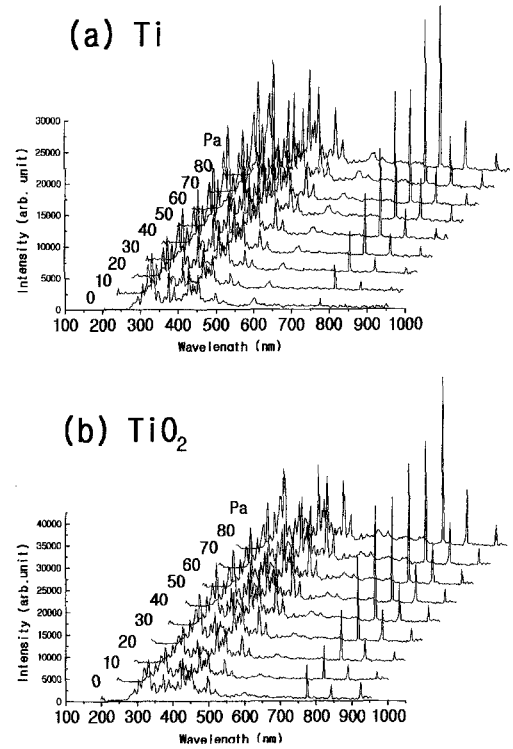

Figure 3. Waterfall graphs of the optical emission spectra of the laser ablation plasma plume of the Ti target (a) and TiO_2 target (b)

The waterfall graphs of the optical emission spectra of the laser ablation plasma plume of Ti and TiO_2 targets versus various buffer gas pressures are shown in figure 3. There are many peaks of Ti I, II in the range of 250 - 500 nm and those of O I in 750 nm as mentioned about figure 2. In the range of 500 - 700 nm, there are many peaks of titanium oxide (TiO), but they are so complicated and diverse as molecule property that they are not separated and assigned into a level. However they do not appear as a sharp peak, the trend is proven that the intensities of peaks are remarkably increased as the buffer gas pressure increased.

3.2 Peaks from atomic Ti and O

The pressure dependences of the intensities for some peaks are shown in figure 4. The indication "0 Pa" means the base pressure of about 3 x 10^{-5} Pa. The filled marks of square, triangle and circle indicate the peaks 323 Ti II $3d^2 4s$ - $3d^2 4p$, 430 Ti I $3d^3 4s$ - $3d^3 4p$ and 777 O I $1s^2 2s^2 2p^3 3s$ - $1s^2 2s^2 2p^3 3p$ in the case of Ti target as shown in the figure 2 and the open symbols indicate in the case of TiO_2 target, respectively. The intensities are normalized by the intensities of peak 295 Ti I $3d^2 4s^2$ - $3d^2 4s4p$, since the peak have comparative small as the exciting transition $3d^2 4s^2$ - $3d^2 4s4p$ is not affected by the buffer gas pressure [13]. The solid and broken lines

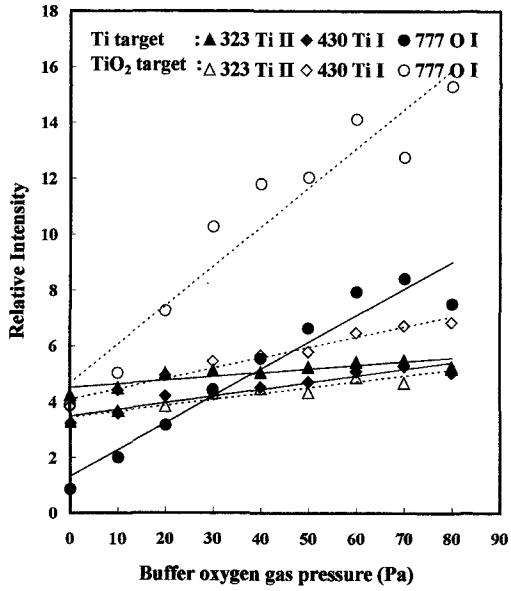

Figure 4. Buffer gas dependence of atomic Ti I, II and O I peak intensities

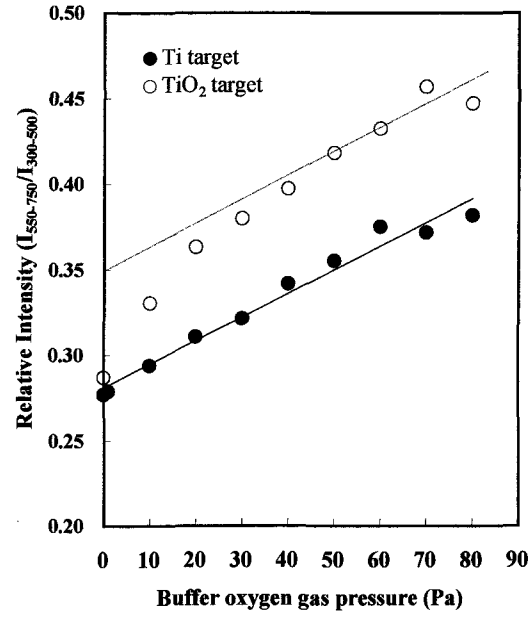

Figure 5. Buffer gas dependence of molecule TiO* peak intensity

indicate approximate liner line for the case of Ti and TiO_2 target, respectively. The trend of the inclination are large in the 777 O I. It must be discussed from the producing process that is separated into two mechanisms [14]. The first mechanism is the photon absorption in the laser ablation and the second is the collision after the bombardment. The first mechanism includes evaporations by absorbing multi photons and plasma heating by inversed bremsstrahlung radiations [15]. These primary sputtering mechanism is general well understood and are not affected by the atmosphere. Here the trends are mainly affected by the collisions.

An excited state of Ti^* and Ti^{+*} is produced by following process;

elastic collision:

$Ti + e$ (or Ti/O) -> $Ti^* + e$ (1)

electron capture:

$Ti^+ + e$ (or Ti/O) -> Ti^* (2)

electron emission from (Auger effect)

Ti^* -> $Ti^{+*} + e$ (3)

There are also the combination of the all element exist in the region.

An excited state of O^* is produced by dissociation of O_2 and TiO_2 in addition to the process in the Ti^* production;

dissociation of dioxide:

$O_2 + e$ (or atom/ion) -> $O^* + O + e$ (4)

$TiO_2 + e$ (or atom/ion) -> $Ti + O^* + O + e$ (5)

In the case of Ti I, the trend shows the increase ratio of the Ti + O_2 collision of the excitation to $3d^24s4p$ (295 Ti I) is smaller than to $3d^34p$ (430 Ti I). In the case of 430 Ti I, the buffer gas dependence of the exciting transition to $3d^24p$ is similar as to $3d^34p$. In both cases, there are not striking difference from the targets. It shows that the production of Ti^* and Ti^{+*} are not well affected by that whether the target is Ti or TiO_2. In the case of O_2, the excited state of O^* is produced both from the target and the buffer gas. The intensity of the emission in the Ti target at 0 Pa is not equal to zero, so it is originated from surface oxides. The difference of the intensity in the TiO_2 and Ti targets is mainly a contribution of O* originated from the targets, so the components proportional to the buffer gas pressure are originated from collisions with buffer gas (eq. (4)).

3.3 Peaks from TiO molecule

There are numerous excited states of titanium oxide (TiO^*) peaks in the spectra, but the peaks from molecule are comparably broader than the peaks from single atom or ion as its complication of the energy levels. Therefore some aggregate treats are necessary for quantitative analysis in the TiO^* peaks. In the astronomy, "the five-colour system" is one of the popular system, that have five filter in the ranges from 781.8 to 1050.6 nm with about 10 nm half-power bandwidth [4]. A plenty of star are analysed by the system, for example [16]. In the PLD, we investigate the rough estimation to compare the integrated intensities on the assumption that the spectral bands around 300 - 500 nm and 550 - 750 nm are almost assigned to be Ti^* and TiO^*, respectively. The plotted graph of integrated dose in the range of 300 - 500 nm ($I_{300\text{-}500}$) and 550 - 750 nm ($I_{550\text{-}750}$) is shown in figure 5. The relative intensities $I_{550\text{-}750}/I_{300\text{-}500}$ consist of three components; the base part, the liner increase part and the non-liner increase part. The base part has the same population possession of the contribution of Ti peaks at the range of 300 - 500 nm, therefore it originates from Ti atom/ion from the target as represented in 590 - 610 nm Ti I. In this treatment, this part is a constant background at the magnitudes of 0.28 in the both case of Ti and TiO_2 targets. The liner increase part is proportional to the ambient dioxide gas pressure in addition to the population of Ti atom/ion from the target. It consists of TiO^* produced by collisions of Ti atom/ion from the target and the ambient dioxide gas. The non-liner

increase part appears only in the TiO_2 target, so it corresponds to the balance of the intensities in the TiO_2 and Ti target. The intensity increases and saturates to a constant value as the ambient dioxide gas pressure increase. It is a contribution of TiO^* produced by interactions between the O atom/ion and Ti atom/ion from the target. In this experiment, the contribution of TiO^* directly from the TiO_2 target was not observed.

4. CONCLUSIONS

The optical emission spectroscopy of the laser plasma plume during PLD is applied to diagnostics of the TiO_2 thin film growths. The peaks of the excited states of Ti^*, Ti^{+*} and O^* were observed and assigned clearly, and the production processes were discussed in qualitatively. Furthermore the buffer dioxide gas pressure dependences of the excited states of TiO^* production were explained in quantitatively.

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