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Spectroscopic Characteristics of Plasma Plume Induced by Laser Ablation of WO_3 Target

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We report on the temporal and spatial resolved spectroscopic characteristics of the tungsten tri-oxide (WO_3) plasma plume generated by Nd:YAG laser ablation. Emissions are dominated by mono-atomic neutral tungsten (W I), and there are no emission species such as W ions, O neutrals and molecular species. W I emission species move with high speed of 8.9×10^3 m/s at the delay time (τ_d) from 200 to 1000 ns after the laser irradiation. Two-dimentional images of expanding plasma plume were observed trough an ICCD camera.

Keywords: Laser ablation, Plasma plume, Tungsten oxide, Optical emission spectroscopy, ICCD image

1. INTRODUCTION

Tungsten oxide (WOx) has been widely studied due to their electrochromic properties for display [1–3]. In addition, WOx is useful as a gas sensor [4]. Several methods have been used to prepare WOx thin films, such as thermal evaporation [5], RF sputtering [6], spray pyrolysis [7], sol–gel [8], and chemical vapor deposition [9, 10]. Compared to these preparation methods, the films deposited by pulsed laser ablation (PLA) show high crystallinity and stoichiometry. In order to fabricate high quality functional thin films and nano-structure materials, it is required to investigate the properties of ablation plumes during the film deposition. Especially, it is important to know the correlation between the properties of the plasma plume and the characteristics of the deposited films. Optical emission spectroscopic (OES) analysis has been used to measure the plasma plume. OES measurement can monitor the in-situ ablation process without the external affect [11].

In this paper, we report on the results from a spectroscopic investigation of the plasma plume by ablating WO_3 target in order to estimate the behavior of the plasma plume, and to prepare high quality WOx thin films. The temporal and spatial distributions and the optical emission species of the plasma plume at various conditions were observed through a spectrometer and an ICCD camera.

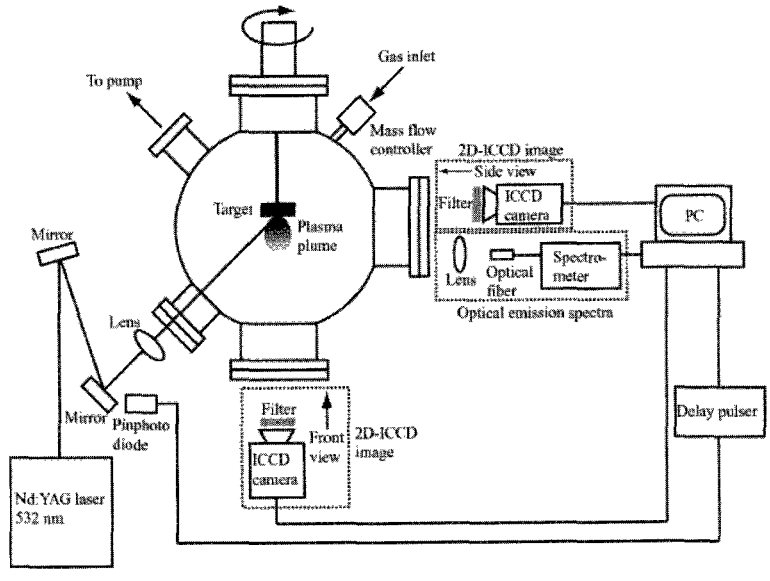


Fig.1 Schematic diagram of the experimental setup.

Tabel I Measurement conditions of spectroscopic characteristics.

Target	WO_3 (purity 99.9 %)
Ambient gas pressure	O_2, Ar 1~30 Pa
Measurement point d away from the target surface	0.5~9 mm
Delay time τ_d after laser irradiation	200~3000 ns
Wavelength	400~420 nm
I.I. Gate width	50 ns
Acquisition No.	16

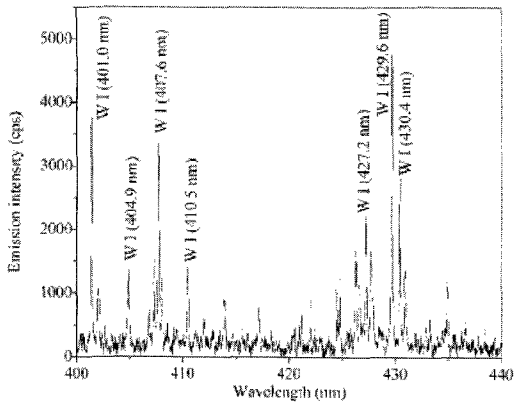


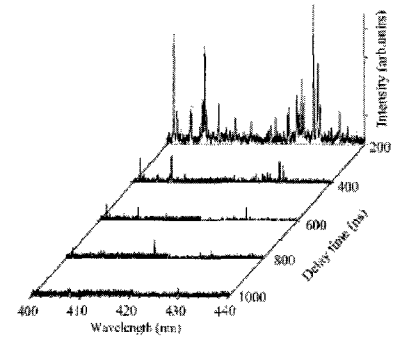
Fig.2 Emission spectrum of the plasma plume produced by ablating WO_3 target at O_2 gas of 10 Pa.

2. EXPERIMENTAL

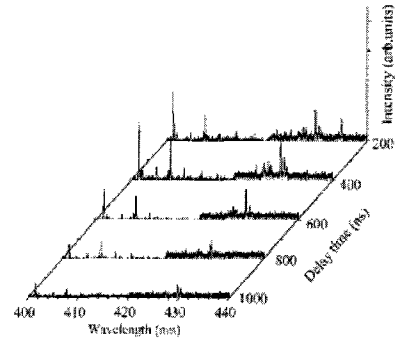
Experimental setup for measuring laser-ablated plasma plumes is shown in Fig. 1. A Nd:YAG laser (Continuum SureliteIII; wavelength of 532 nm, pulse duration of 3.5 ns, maximum output energy of 340 mJ) was used for ablating WO_3 target. The vacuum chamber was evacuated to a base pressure of 4×10^{-4} Pa by a turbomolecular pump, and then filled with ambient gases at a flow rate of 20 sccm. Optical emission spectra were recorded through a spectrometer (Hamamatsu C5095) equipped with an ICCD camera (Hamamatsu C7164-03) by varying delay time (τ_d) and distance (d) away from the target. Two-dimensional plasma emission images were observed through an ICCD camera. Table I shows the measurement conditions of the spectroscopic characteristics.

3. RESULTS AND DISCUSSION

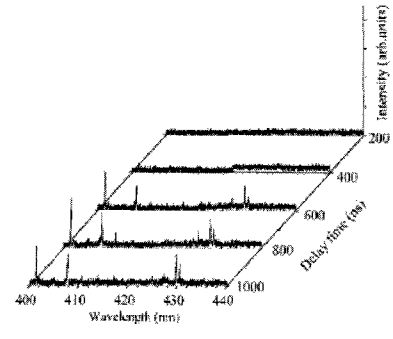
Figure 2 shows the optical emission spectrum of the plasma plume produced by ablating WO_3 target in O_2 gas of 10 Pa at d=0.5 mm from the target. Some emission lines which are identified mono-atomic neutral tungsten (W I) are observed. However, W ions, O neutrals and molecular species are not detected regardless of the measurement conditions. Therefore it seems that the oxidation reaction of W occurred on the substrate surface. Temporal and spatial behavior



(a) d=0.5 mm



(b) d=2 mm



(c) d=5 mm

Fig.3 Temporal evolution of WO_3 ablation plume as parameters of delay time (τ_d) from 200 to 1000 ns and distance (d) from the target.

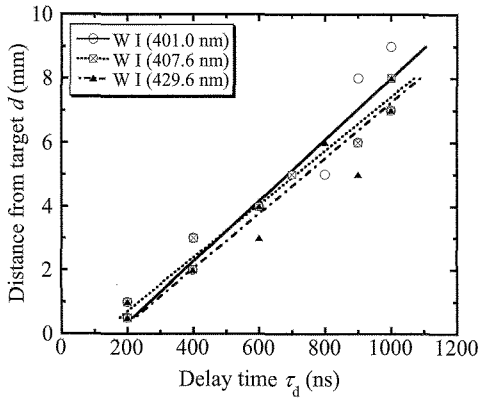


Fig.4 The d-τ_d plots of W I (401.0, 407.6 and 429.6 nm).

of emission lines at d=0.5~5 mm from the target at τ_d=200~1000 ns after the laser irradiation are shown in Fig. 3. The strong emission spectrum at d=0.5 mm is observed at τ_d=200 ns, although it becomes weak rapidly. The peak intensity at d=2 and 5 mm is maximum at τ_d=400 and 600 ns, respectively. It was found that the emission of the plasma plume moved forward from the target. For three emission lines of W I (λ=401.0, 407.6, 429.6 nm) in Fig. 3, the relationship between the distance (d) and delay time (τ_d) when the intensity is at a maximum is shown in Fig. 4.

The estimated velocity of W I is about 8.9×10^3 m/s (kinetic energy ~76 eV) and W I species reach to the substrate with high energy. At later delay time (τ_d=1000~), W I velocity became saturate because that emission species in the plasma plume loose the kinetic energy by collisions with the ambient gas molecular.

Figure 5 shows time-resolved WO_3 plasma plume emission in O_2 and Ar of 1~30 Pa at τ_d=110~3000 ns. All of the images are normalized to the maximum intensity. The plume expansion was observed up to 1 μs at O_2 gas of 1 Pa. However as the pressure was increased, the plume was observed at longer delay time due to increase of the lifetime of excited species in the plasma plume. The front velocity of the plasma plume at O_2 gas of 10 Pa is about 6.0×10^3 m/s, which is in an approximate agreement with the result estimated in Fig.4. The plasma plume expansion in an inert Ar gas of Fig.5 is smaller than that in O_2 gas.

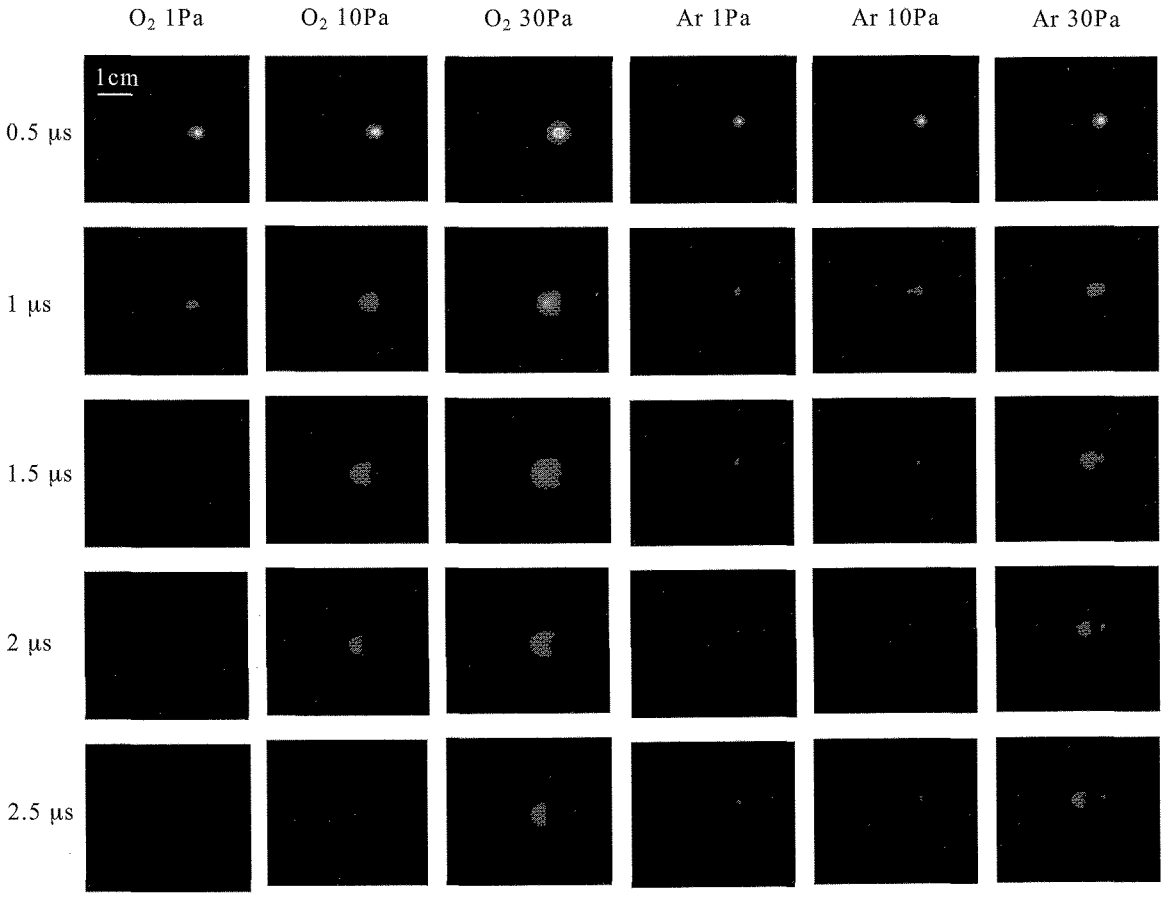


Fig.5 ICCD images of WO_3 plasma plume imaging taken at delay time (τ_d) of 0.5~2.5 μs after the laser irradiation.

CONCLUSIONS

We have characterized the WO_3 laser ablation plume in O_2 and Ar gas of 1~30 Pa. Optical emission spectra from the plasma plume showed the presence of W I. The velocity of W I was estimated to be about 8.9×10^3 m/s. The ICCD images of the expanding plasma plume revealed that the lifetime of excited species in the plasma plume became longer with increasing gas pressure.

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