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Study on the behavior of the Plasma Plume and Film Quality using Pulsed Laser Deposition with Tungsten Target

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Temporal and spatial behavior of WO_3 plasma plume in pulsed laser deposition process have been studied using emission spectroscopic method. Three dimensional study of the plasma plume suggested that the emission plasma plume grew toward substrate direction after the laser irradiation on the target to 2.0 μs, and they disappeared gradually. Emission from the tungsten atoms was dominated in the plasma plume, and there was no emission species such as W ions, O neutrals and molecular species in the plasma plume. W I emission species move with high speed of 5~9 km/s at the delay times (τ_d) from 0.5 to 2.0 μs after the laser irradiation on the tungsten target surface. We also prepared WO_x thin films on flexible ITO substrates by PLD method, and it is confirmed that they worked as electrochromic display.

Key words: plasma, nano-materials, superfluidity, helium, liquid

1. INTRODUCTION

Tungsten oxide (WO_x) is widely used materials for hard coating, gas sensor and electrochromic display [1–4]. Therefore, WO_x thin films have been prepared using thermal evaporation [5], RF sputtering [6], spray pyrolysis [7], sol–gel [8], and chemical vapor deposition [9-11]. We also prepared WO_x films on the solid glass substrates using pulsed laser deposition (PLD) method because of their advantages of a simple system setup, wide ranging deposition conditions, a wider choice of materials, higher instantaneous deposition rates, high reproducibility and high crystallinity[12-14].

On the other hand, flexible electrochromic displays are required, such as organic electroluminescence displays, liquid crystal displays and paper-like displays. Therefore, we have been prepared WO_x thin films on the flexible substrate. However, the film quality is not high enough to use electrochromic display.

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.

In this paper, optical emission spectroscopic (OES) study of the plasma plume by ablating WO_3 target have been performed in order to estimate the behavior of the plasma plume and prepare high quality WO_x thin films. 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. We also prepare WO_x films for the electrochromic display, and compare with the emission spectra and the behavior of the plasma plume and film quality.

2. EXPERIMENTAL

A schematic for measuring laser-ablated plasma plume 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 the oxygen gas 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 time delay (τ_d) after the laser irradiation and distance (d) away from the target surface. Two-dimensional plasma emission images were observed through an ICCD camera. Table 1 shows the

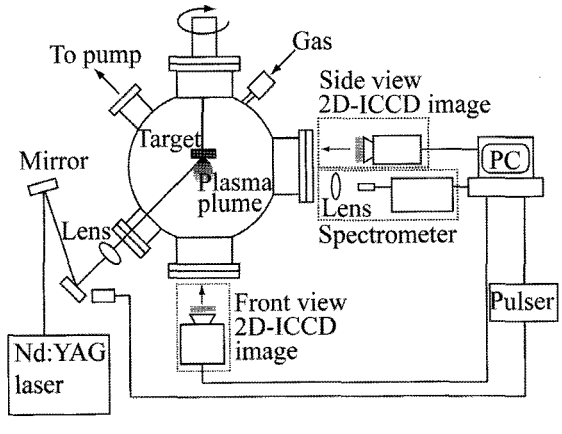


Fig. 1 A schematic for measuring laser-ablated plasma plume.

Tabel 1 Measurement conditions of spectroscopic characteristics.

Target	WO_3 (purity 99.9 %)
Ambient gas pressure	O_2, 10~30 Pa
Measurement point d away from the target surface	0.5~9 mm
Delay time τ_d after laser irradiation	200~3000 ns
Wavelength	400~440 nm
I.I. Gate width	50 ns
Acquisition No.	16

conditions of the spectroscopic measurement.

The substrate in these experiments was flexible indium tin oxide substrate (OTEC, Tobi Co., Ltd.) and was located at 6.0 cm from the target. The substrates were cleaned using an ultrasonic agitator by repeated bathing and were then rinsed in high-purity deionized water prior to loading into the deposition chamber.

The transmittance of the solution was measured using a Hitachi UV-3300 spectrometer.

3. RESULTS AND DISCUSSION

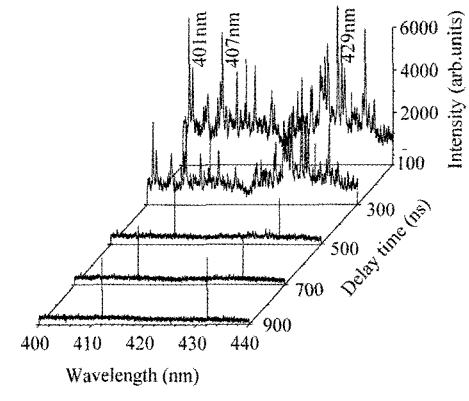
3.1 OES study in the plasma

Figure 2 shows the temporal evolutions of optical emission spectra of the plasma plume from WO_3 target in O_2 gas of 20 Pa at d=0.5, 3.0 and 5.0 mm from the target. Optical emission spectra showed the presence of mono-atomic neutral tungsten atoms (W I). However, W ions, O neutrals atoms and molecular species are not detected in this condition. These results suggest that the oxidation reaction of W was caused on the substrate surface. Temporal and spatial behavior of emission lines at τ_d=100~900 ns after the laser irradiation suggest that the strong emission spectrum at d=0.5 mm is observed at τ_d=100 ns, although it becomes weak rapidly after that. The peak intensity at d=3 and 5 mm is maximum at τ_d=300 and 700 ns respectively. These results suggest that the emission plasma plume moved forward from the target.

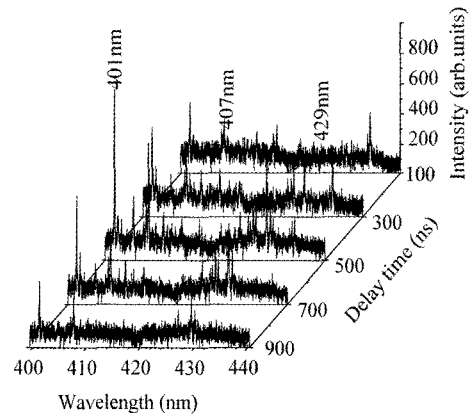
Fig. 3 shows the velocity of W I (λ=401.0, 407.6, 429.6 nm) calculated from some relationships between the distances (d) and time delays (τ_d) of the maximum intensity calculated from Fig. 2. The estimated velocities were about 5~9 km/s, and they reach to the substrate with high speed and high energy. At later time delays (τ_d =1000~), W I velocities become saturated because that emission species in the plasma plume loose the kinetic energy by collisions to the ambient gas molecular, not shown here.

3.2 Behavior of the plasma plume

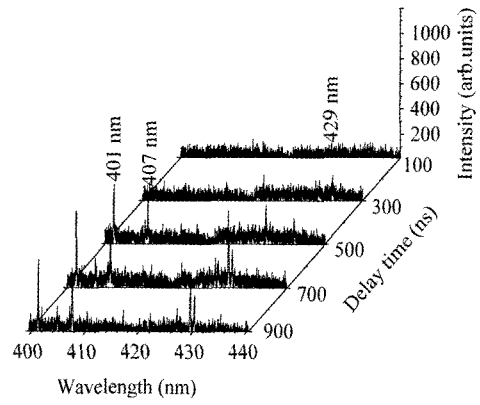
Figure 4 shows temporal evolutions of two dimensional WO_3 plasma plume emission in O_2 of 10~30 Pa at τ_d=0.5~2.0 μs. All of the images in Fig. 4 are normalized to the maximum intensity in that image. The plume grew up to 1.5 μs, and then they contract at the gas pressure of 20 Pa. This tendency is strongly depend on the gas pressure, The plasma plume expansion in an inert Ar gas is smaller than that in O_2 gas. The growth velocity of the plasma plume, estimated from the side view of the plasma plume is about 3.0km/s



a) d=0.5mm



b) d=3.0mm



c) d=5.0mm

Fig. 2 Temporal evolutions of optical emission spectra of the plasma plume from WO_3 target in O_2 gas of 20 Pa at d=0.5, 3.0 and 5.0 mm from the target.

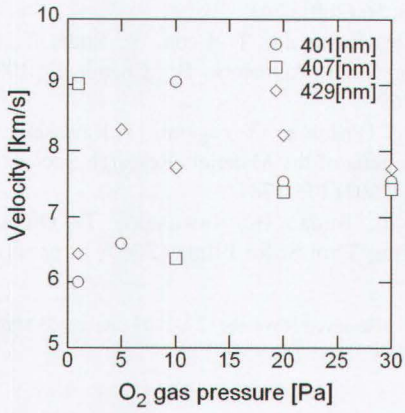
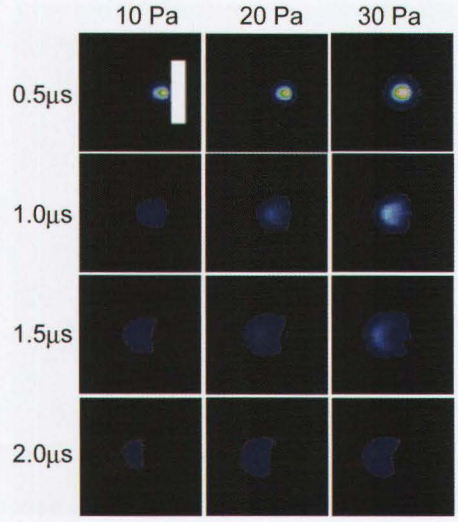
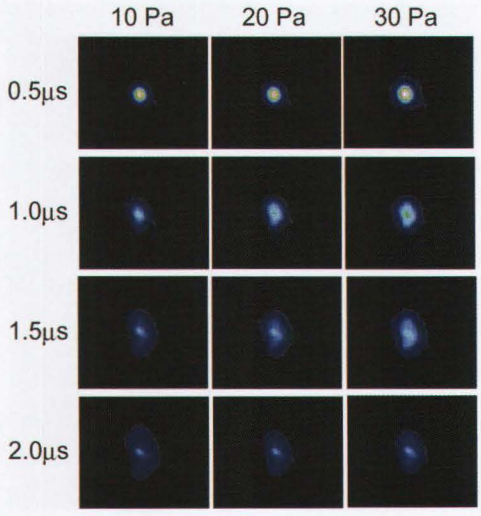


Fig. 3 Velocity of W I (λ=401.0, 407.6, 429.6 nm) calculated from some relationships between the distances (*d*) and time delays (τ_d).



(a) Side view of the plasma plume



(b) Front view of the plasma plume

Fig. 4 Temporal evolutions of two dimensional WO_3 plasma plume emission in O_2 of 10~30 Pa at τ_d=0.5~2.0 μs.

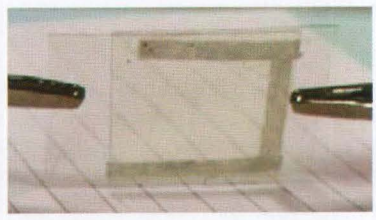
at O_2 gas of 20 Pa. This result roughly agrees with the result estimated in Fig. 3. Intensity of the light emission and life time of the plasma plume increased with increasing gas pressure as shown in Fig. 4. This may be due to increasing of the lifetime of excited species in the plasma plume by collisions.

3.3 Film quality measurement

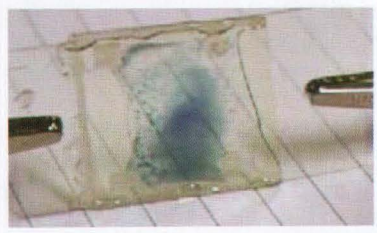
Figure 5 shows photographs of the electrochromic cell prepared using WO_3 thin film synthesized by PLD method. WO_3 thin films are prepared on the flexible ITO substrate (bottom ITO electrode), and liquid electrolytes of 1 mol/liter $LiClO_4$ propylene carbonate/ethylene carbonate (PC DME (1:1 v/v%) Kishida Chemical Co., Ltd.) are placed on the WO_3 films. After that, the films are sealed by more of the flexible ITO substrate (top ITO electrode).

To study the electrochromic property, a DC voltage of 3 V was applied between the top and bottom ITO electrodes. The transparent electrochromic film changed to blue after applying the DC voltage. This may be due to a transfer of film property as follows. In the stoichiometric WO_3 system, the tungsten ion has a valence state of W^{6+}. However, the insertion of Li^+ ions into the amorphous WO_3 results in a W^{6+}/W^{5+} mixture valence state. Light absorption ranging from approximately red to infrared is caused by electron exchange between adjacent W^{6+} and W^{5+} states and, consequently, the color of Li_xWO_3 changes from transparent to blue.

Figure 6 shows the visible light transmittance spectra of the film fabricated by PLD method. Transmittance of the film increased from 380nm with wavelength and they are almost constant



(a) Before applied voltage



(b) After applied voltage

Fig. 5 Photograph of the electrochromic films prepared using WO_3 thin films.

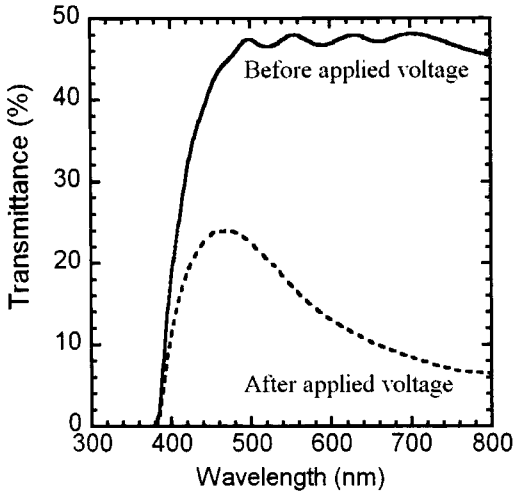


Fig. 6 Visible light transmittance spectra of the flexible electrochromic film.

after 500nm. However, they decrease with increasing wavelength after applying a DC voltage. This tendency also suggests that the color changes from transparent to blue by applying a DC voltage.

4. CONCLUSION

We have characterized the WO_3 laser ablation plume in O_2 gas. Optical emission spectra from the plasma plume showed the presence of mostly W I. The velocity of W I was estimated about 5~9 km/s. The two dimensional images of the plasma plume revealed that they grow up to 1~2 μs. We also prepared WO_x thin films on flexible ITO substrates by PLD method, and it is conformed that they worked as electrochromic display.

5. References

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