

# Thin-Film Growth of Oxides Including Alkaline Metal by Pure Ozone

## Background

Pulsed-Laser Deposition (PLD) technique [Fig.1] has rapidly extended its applicable area, and now it is widely accepted as a technique to precisely control chemical composition and structure of films. Unfortunately, it has been difficult to apply this technique to oxides including alkaline metal because of its extremely high vapor pressure. However, the recent rapid development of oxide materials for practical use, *e.g.* optical device, indicates the necessity to establish the PLD-growth technique for alkaline metal including oxides.

## Purpose

Through the study of PLD growth of LiNbO<sub>3</sub> thin films, we analyze how and when the deviation of chemical composition occurs, and propose to use ozone (O<sub>3</sub>) as an oxidant instead of molecular oxygen (O<sub>2</sub>) to improve the controllability of chemical composition.

## Principal Results

We resolved the PLD process into three parts as shown in Fig.2 and studied how the deviation of chemical composition occurred in each part. When we applied the typical growth conditions of conventional PLD *i.e.* the ablation in 1 - 10 Pa molecular oxygen, the ablated elements were seriously scattered by the oxidant gas before reaching the substrate [Film A], resulting in the deviation of chemical composition. Even if we simply reduced the oxygen pressure, we could not suppress the re-evaporation of Li from the substrate [Film B]. Therefore, we switched the gas to O<sub>3</sub> and simultaneously reduced the pressure during the growth [Film C].

### 1. Suppression of the deviation of chemical composition

We succeeded in obtaining nearly stoichiometric LiNbO<sub>3</sub> ([Li]:[Nb] = 1:1) from a stoichiometric target, which was supported by X-ray diffraction as shown in Fig.3. The essential points of the improvement were as follows;

- (1) Reduction of gas pressure suppresses the scattering of ablated species [Fig.2(b)],
- (2) High activation of ozone suppresses the re-evaporation of Li [Fig.2(c)].

In addition, it was confirmed that the deviation of chemical composition at the target surface is not significant in Li-including oxides. However, it should be noted that this is not necessarily true for Na and K-including oxides, where the deviation of chemical composition is significant at the ablation process (sputtered out of the target). For these materials, further optimizing of the growth condition including laser power is necessary.

### 2. Surface morphology of the LiNbO<sub>3</sub> thin film

We found accidentally that the film grown by ozone has an extremely flat surface as shown in Fig.4 [Film C]. This feature may open the way to fabricate much more complicated structures such as superlattices and/or multilayers. Our next step is to demonstrate that LiNbO<sub>3</sub> can be used for such a nanotechnology application.

## Future Developments

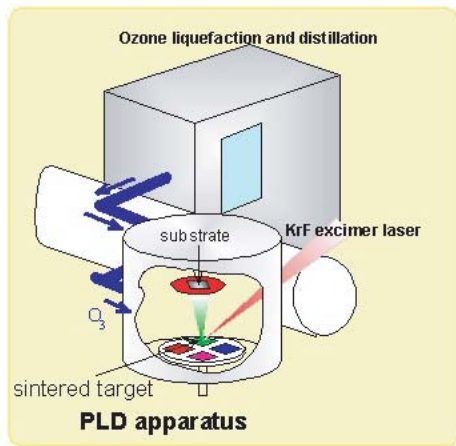
As is widely known, the application area of Li-including oxides is huge; they are useful for electric power applications *e.g.* CO<sub>2</sub> separation in Solid Oxide Fuel Cell (SOFC), which implies that the role of these materials will become more important in the near future. We hope that the present technique will be applied to various materials.

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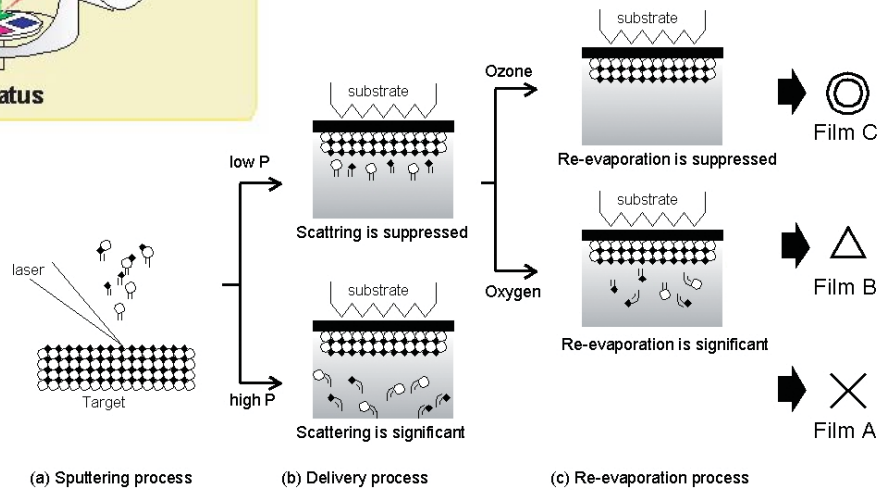
Research Scientist, Materials Physics and Synthesis Sector, Materials Science Research Laboratory

## Reference

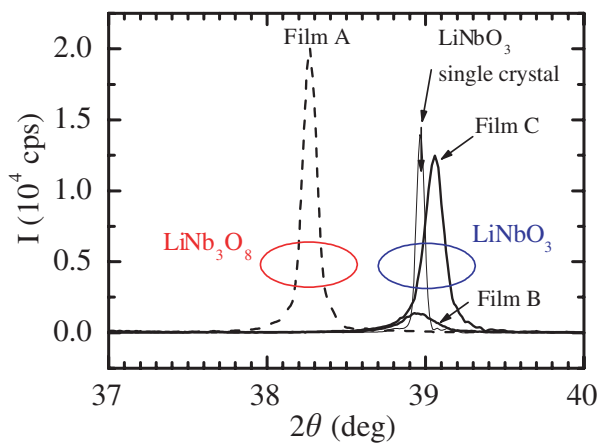
- 1) "Pulsed-Laser Deposition of LiNbO<sub>3</sub> Thin Films at Low-Oxidation Gas Pressure with Pure Ozone", Jpn. J. Appl. Phys. 42, L1066-L1068 (2003).
- 2) "Pulsed-Laser Deposition of LiNbO<sub>3</sub> in Low Gas Pressure Using Pure Ozone", Jpn. J. Appl. Phys. 43, 5307-5312 (2004).



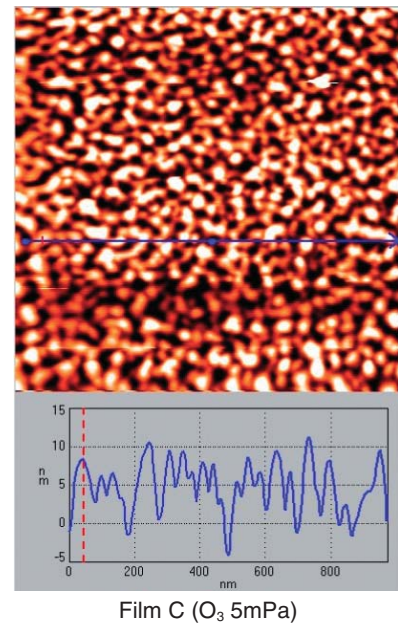
**Fig.1** PLD apparatus. Thin-film sample is obtained by crystallization of metal elements, which are sputtered by laser from the sintered target, onto the substrate with oxidant gas introduced into the vacuum chamber.



**Fig.2** The deviation of chemical composition can occur (a) when atoms or molecules are sputtered out of the target, (b) when the ablated species are delivered to the substrate in the oxidant gas, and (c) when the re-evaporation occurs during the crystallization on the substrate. Decrease of the gas pressure improves mainly process (b), while ozone effectively improves mainly process (c).



**Fig.3** X-ray diffraction of three  $\text{LiNbO}_3$  thin films. Film A shows a Li-deficient structure ( $\text{LiNb}_3\text{O}_8$ ) while the other films exhibit a structure of nearly stoichiometric  $\text{LiNbO}_3$ . By comparing Films B and C, we can see that the crystallographic quality becomes better when grown in  $\text{O}_3$ .



**Fig.4** Atomic-force microscopy image of Film C. Only nm-scale roughness is observed in  $1\mu\text{m}^2$  area indicating an excellently flat surface.