Diversity in plasma arrival sequence correlated to oxygen deficiencies of oxide thin films grown by PLD

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Oxide thin films grown in vacuum by pulsed laser deposition (PLD) are usually oxygen deficient, due to the well-known reasons such as preferential plasma scatterings or resputtering. The present work demonstrates another possibility that results in oxygen deficiencies associated to the much earlier arrival of O^+ as compared to other cation ions. The earlier arrived O^+ cannot be independently deposited as solid without other cation constituents. In particular, this effect is pronounced when performing PLD using a 248 nm laser, with a large proportion of O^+ generated via a 3-photon ionization process during the initial laser solid interactions.

Pulsed laser deposition (PLD) is one of the most commonly applied deposition techniques, that is possible to realize a congruent growth of oxide thin films with complex compositions [1–10]. PLD transfers the target composition as thin films via laser-induced plasma plume in vacuum or under background partial pressures [1,4–6]. In most cases, the growth of oxide thin films is performed under oxygen containing circumstance in order to avoid the deficiency of oxygen in the oxide thin films, since the thin film grown in vacuum or quasi-vacuum ($\leq 10^{-3}$ mbar) is usually oxygen deficient. In vacuum, the plasma species possesses a large kinetic energy (E_k) up to several hundreds of eV [4–6], which is sufficient to re-sputter the film elements with a preference of lighter composition [7,8]. Meanwhile, the plasma elements can be recoiled or backscattered by the surface of the as-grown film, which is also in preferential for the lighter plasma constituents [9]. These well explain the oxygen deficiency in the oxide thin films grown in vacuum, since oxygen possesses a smaller atomic weight than most of other cation elements [5,6]. Nevertheless, there are also some cases that the desired oxide thin film properties cannot be achieved when using high background partial pressures.

In the present work, we show that apart from the above already known causes, the arrival time and sequence of different plasma species can also result in oxygen deficiency in the oxide thin films prepared by PLD in vacuum. Tak-

ing representative examples from vacuum depositions of $Ca_3Co_4O_9$ and $La_{0.6}Sr_{0.4}MnO_3$ (LSMO), we derive the arrival times of the main ionic plasma species from their kinetic energy distributions. It gives a new insight into why there is oxygen deficiency in the oxide thin films prepared by PLD in vacuum, by comparing the diversity in the arrival sequence of oxygen and other cation plasma species.

Table 1 summarizes the composition of $Ca_3Co_4O_9$ [6] and $La_{0.6}Sr_{0.4}MnO_3$ [4,5] thin films grown in vacuum or quasi-vacuum by PLD. It can be obviously seen that the deficient oxygen compositions in $Ca_3Co_4O_9$ and $La_{0.6}Sr_{0.4}MnO_3$ thin films grown using a KrF excimer laser ($\lambda = 248$ nm), as well as $La_{0.6}Sr_{0.4}MnO_3$ thin film grown using an ArF excimer laser ($\lambda = 193$ nm). In contrast, the $La_{0.6}Sr_{0.4}MnO_3$ thin films grown using the same laser ablation fluence but a XeCl excimer laser ($\lambda = 308$ nm) shows an oxygen composition almost reaching the stoichiometric number. The diversity in composition of the as-grown $La_{0.6}Sr_{0.4}MnO_3$ thin films using various laser wavelengths further influences the crystal structures. For example, a strong diffraction peak from an epitaxial grown and crystallized LSMO film is observed for the deposition using $\lambda = 308$ nm, which is not achievable for the deposition using $\lambda = 248$ nm or 193 nm [4].

The oxygen deficiency was attributed to the high kinetic energy of the plasma species [1], which can be also observed from the E_k distributions for the main ionic plasma species when growing $Ca_3Co_4O_9$ and $La_{0.6}Sr_{0.4}MnO_3$ in vacuum [4–6]. However, this can not explain why the $La_{0.6}Sr_{0.4}MnO_3$ thin film grown in vacuum by using a 308 nm laser shows a nearly stoichiometric oxygen composition. It is worth to be noted that the cation ions show a similar E_k when ablating $La_{0.6}Sr_{0.4}MnO_3$ using $\lambda = 308$ and $\lambda = 248$ nm in vacuum [4].

Herein, we investigate the ionic plasma properties from a different aspect by looking at the time of arrival (TOA) distributions and the arrival sequence of the main ionic plasma species. The E_k distribution represents the variation in relative numbers of the ionic plasma species as a

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Table 1 Summary of the composition of $\text{Ca}_3\text{Co}_4\text{O}_9$ [6] and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ [4,5] thin films grown in vacuum or quasi-vacuum using different laser ablation conditions

Target material	Deposition background	Laser ablation condition	Thin film composition	Loss of oxygen
$\text{Ca}_3\text{Co}_4\text{O}_9$	$<10^{-6}$ mbar	$\lambda = 248$ nm; $F = 1.5$ J cm^{-2}	$\text{Ca}_{2.9}\text{Co}_{4.0}\text{O}_{7.1}$	21%
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	$<10^{-6}$ mbar	$\lambda = 248$ nm; $F = 1.8$ J cm^{-2}	$\text{La}_{0.60}\text{Sr}_{0.38}\text{Mn}_{0.93}\text{O}_{2.7}$	10%
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	2×10^{-3} mbar	$\lambda = 248$ nm; $F = 1.8$ J cm^{-2}	$\text{La}_{0.6}\text{Sr}_{0.40}\text{Mn}_{0.97}\text{O}_{2.7}$	10%
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	$<10^{-6}$ mbar	$\lambda = 308$ nm; $F = 1.8$ J cm^{-2}	$\text{La}_{0.60}\text{Sr}_{0.42}\text{Mn}_{0.95}\text{O}_{3.0}$	0%
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	$<10^{-6}$ mbar	$\lambda = 193$ nm; $F = 1.8$ J cm^{-2}	$\text{La}_{0.60}\text{Sr}_{0.38}\text{Mn}_{0.98}\text{O}_{2.8}$	6.7%

function of E_K , known as $\text{d}N/\text{d}E_K$ [10]. While the TOA distribution indicates the variation in relative numbers of the ionic plasma species with respect to its arrival time, known as $(\text{d}N/\text{d}t)$ [10]. In vacuum, the plasma species is expected to freely expand without experiencing effective scatterings by the background molecules. The scattering between the freely expand electrons is not expected to significantly change the momentum of the plasma species due to the much smaller mass of electrons than the atomic or ionic plasma species. In addition, the laser pulse duration (around 20 nanoseconds) is much shorter than the plasma propagation time (around a few microseconds), which indicates a shorter time is required for the plasma generation as compared to the plasma propagation. Therefore, the TOA distribution ($\text{d}N/\text{d}t$) can be converted from the E_K distribution ($\text{d}N/\text{d}E_K$) using the following correlation:

$$\frac{\text{d}N}{\text{d}t} = \frac{(2E_K)^{3/2}}{m^{1/2}d} \times \frac{\text{d}N}{\text{d}E_K},$$

where m represents the atomic weight of the ionic species, while d is the plasma propagation distance. Fig. 1 shows the derived TOA distribution for the main ionic plasma species when ablating $\text{Ca}_3\text{Co}_4\text{O}_9$ (Fig. 1a) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (Fig. 1b) using a 248 nm lasers. The most probable arrival time (t_{MP}) is obtained when the $\text{d}N/\text{d}t$ shows the maximum number. For both depositions, a considerable amount of O^+ was observed. These O^+ arrives at the substrate much earlier than other cation ions.

Apart from the above demonstrated arrival time directly converted from E_K into TOA distribution, the arrival sequence of the different plasma species can be also estimated using their average arrival time ($t_{\text{Avr.}}$). The $t_{\text{Avr.}}$ is derived from the average kinetic energy ($E_{K, \text{Avr.}}$) by

$$t_{\text{Avr.}} = d / \sqrt{2E_{K, \text{Avr.}} / m} \quad [6].$$

The $E_{K, \text{Avr.}}$ is derived from the E_K distribution ($\text{d}N/\text{d}E_K$) of the specific ionic plasma species by

$$E_{K, \text{Avr.}} = \int \frac{\text{d}N}{\text{d}E_K} E_K \text{d}E_K / \int \frac{\text{d}N}{\text{d}E_K} \text{d}E_K \quad [6].$$

Figure 1 TOA distribution of the main ionic plasma species when ablating (a) $\text{Ca}_3\text{Co}_4\text{O}_9$ and (b) $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ in vacuum using a 248 nm laser.

In Fig. 2, the derived t_{MP} as well as the $t_{\text{Avr.}}$ is shown for the main ionic plasma species when ablating $\text{Ca}_3\text{Co}_4\text{O}_9$ (Fig. 2a) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (Fig. 2b) in vacuum using a 248 nm laser. A smaller arrival time of O^+ as compared to the cation ions is always observed. Without the presence of the cation elements, it is not possible to stabilize the oxygen species by forming chemical bond. Therefore, it is more difficult to independently stabilize the early arrived O^+ as solid, which may causes the deficiency in oxygen composition of the as-grown thin films. In contrast, the O^- is not expected to cause similar problem since it arrives later than the cation ions due to a smaller E_K of O^- . It is worth to be noted that the as-grown $\text{Ca}_3\text{Co}_4\text{O}_9$ in vacuum shows a

Figure 2 The most probable arrival time (t_{MP}) derived from the TOA distribution as well as the average arrival time ($t_{\text{Avr.}}$) of the main ionic plasma species detected in 248 nm laser ablated (a) $\text{Ca}_3\text{Co}_4\text{O}_9$ and (b) $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.

more significant oxygen deficiency, which is in agreement with the larger proportion of O^+ , $\text{O}^+ / (\text{O}^+ + \text{O}^-)$, observed for laser induced plasma of $\text{Ca}_3\text{Co}_4\text{O}_9$ (86%) as compared to the one of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (39%). In addition, the previous discussion is based on single pulse ablation, which is different from the practical deposition condition by using a continuous laser ablation process using 5 Hz. The ablation frequency of 5 Hz indicates that 200 millisecond is between each laser pulse, which is much longer than the plasma propagation time around several microseconds. Therefore, the practical continuous laser ablation process is expected to result in the same effect to the previous discussions on single pulse ablation.

The above understanding well explains the larger oxygen composition observed in the as-grown $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ in vacuum using a 308 nm laser than in the one grown using 248 or 193 nm lasers. Fig. 3a shows the relative number of O^+ as compared to the sum in amount of O^+ and O^- when ablating $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ in vacuum using $\lambda = 308$, 248 and 193 nm lasers at the same fluence. The shown $\text{O}^+ / (\text{O}^+ + \text{O}^-)$ ratios are derived from ref. [4]. When using $\lambda = 308$ nm, the plasma contains small proportions of O^+ , while equivalent amount O^+ and O^- are observed for using $\lambda =$

Figure 3 (a) Relative amount O^+ ion as compared to the sum of O^+ and O^- and (b) the average arrival time ($t_{\text{Avr.}}$) when ablating $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ in vacuum using 308 nm, 248 nm and 193 nm lasers at the same fluence of 1.8 J cm^{-2} .

248 or 193 nm. The much lower O^+ content in the plasma when using laser with $\lambda = 308$ nm may be associated to its smaller photon energy (4 eV) as compared to the situation when using lasers with $\lambda = 248$ nm (5 eV) or $\lambda = 193$ nm (6.4 eV). Since the first ionization energy for atomic oxygen is around 13.6 eV, it requires a 3-photon process to ionize O into O^+ for using $\lambda = 248$ or 193 nm lasers, while a 4-photon process is needed for using $\lambda = 308$ nm laser. Providing the same laser ablation energy, a 4-photon process is less likely to occur as compared to a 3-photon one, which explains the much smaller amount of O^+ for using $\lambda = 308$ nm as compared to $\lambda = 248$ or 193 nm. The average arrival time for the main ionic plasma species when ablating $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ targets using three laser wavelengths is summarized from ref. [4] and compared in Fig. 3b. An earlier arrival time of O^+ than other cation ion is observed for using all three laser wavelengths. The plasma contains very low proportion of O^+ using $\lambda = 308$ nm, therefore, the oxygen deficiency caused by the earlier arrival of O^+ than other cation ions is expected to be less significant using laser with $\lambda = 308$ nm as compared to the lasers with $\lambda = 248$ or 193 nm. The less significant oxygen deficiency observed in $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ thin films grown by using laser with $\lambda =$

308 nm than the ones with $\lambda = 248$ or 193 nm is in agreement with this finding.

To summarize, a much earlier arrival time of O^+ as compared to other cation ions is observed when growing $La_{0.6}Sr_{0.4}MnO_3$ as well as $Ca_3Co_4O_9$ in vacuum using 248 nm laser. The early arrival oxygen is difficult to be well stabilized as solid, which may cause the oxygen deficiency in the as-grown oxide thin films by PLD in vacuum. This finding is well supported by the larger oxygen composition in $La_{0.6}Sr_{0.4}MnO_3$ grown with a 308 nm laser as compared to the one using 248 or 193 nm. A low content of O^+ is observed in the plasma when ablating the target using a 308 nm laser, since it requires a 4-photon process to ionize atomic oxygen. In contrast, a 3-photon process is required using lasers with $\lambda = 248$ or 193 nm to ionize atomic oxygen and half of the ionic oxygen species are observed in positive charge. The present work provides a new insight into why the loss of oxygen composition easily occurs in the oxide films prepared by PLD in vacuum.

Received 11 February 2015; accepted 16 March 2015;
published online 10 April 2015

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Acknowledgments This work was supported by Beijing Natural Science Foundation (2151004).

Authors contributions Chen J performed the investigation and wrote the paper with support from Chen N. Chen J, Bai Y and Chen N contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 利用脉冲激光沉积法在真空条件下生长的氧化物薄膜通常存在氧元素缺失现象. 在以往研究中, 上述氧元素缺失的原因被归结于等离子体中较轻的氧离子更易被散射或薄膜中的氧元素更易被高能量等离子体再溅射等. 本文提出了真空下脉冲激光沉积氧化物薄膜中造成氧元素缺失的另一个可能原因: 由于等离子体中 O^+ 离子到达衬底的时间早于金属离子, 较早到达的氧元素不能单独在衬底上以固体形式沉积, 从而造成薄膜氧元素的缺失. 当使用波长为248 nm的脉冲激光时, O^+ 离子通过三光子过程大量产生, 证实了上述原因.