Plasma interactions with the N₂O background gas: Enhancing the oxidization of alkaline-earth species for pulsed laser deposition

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Using N₂O as an alternative background gas to O₂ when growing oxide thin films by pulsed laser deposition (PLD) was previously expected to result in larger oxygen contents of as-grown thin films. In this work, we investigate the composition and kinetic energy of the pulsed laser induced plasmas that propagated in N₂O and O₂ by using mass spectrometry and plasma imaging. Two distinguished features were observed when using N₂O instead of O₂. (1) In N₂O background gas as compared to O₂, a larger proportion of negative oxygen ions was detected. (2) The alkaline-earth elements were fully oxidized in the N₂O background, which is not achievable in O₂. These observations are attributed to the smaller dissociation energy of the N₂O molecules as compared to O₂. The smaller dissociation energy of the background gas molecule is expected to reduce the interaction strength during their central collisions with the plasma species. As a result, the dissociable or electron detachable plasma species can be formed in larger amounts in N₂O background, compared to O₂. Comparing the composition of the deposited thin films indicates a larger oxygen content of the film grown in N₂O background gas, as compared to O₂, at pressures of $\sim 10^{-1}$ mbar, which is the most commonly used deposition pressure in PLD. Nevertheless, this was not achieved when performing PLD at $\sim 10^{-2}$ mbar, since the pressure was not high enough to trigger the formation of the shockwave front during the plasma expansion and thereby the lightest oxygen plasma species were preferentially scattered. Published by AIP Publishing. <https://doi.org/10.1063/1.5039998>

I. INTRODUCTION

Pulsed laser deposition (PLD) is one of the most commonly applied and versatile thin film deposition techniques, when growing oxide thin film materials that exhibit complex compositions and/or crystal structures.^{1–31} To compensate the loss in the oxygen composition during a PLD process, an oxygen containing background gas was usually used to modify the physical and chemical properties of the laser induced plasma plume before reaching the substrate.^{1,2} Apart from O₂, more reactive gases such as N₂O were also used as alternative background gas when performing PLD, in which situations higher oxygen contents for specific oxide thin film materials^{4–24} were achieved. Compared to the one of O₂ (~ 5.12 eV), the dissociation energy ($E_{\text{Dissoc.}}$) of the N₂O molecule is smaller (~ 1.6 eV).^{4–6} For example, an electron impact collision is typically expected to result in the dissociation of the background molecules, as: $e^- + \text{O}_2 \rightarrow \text{O} + \text{O} + e^-$, and $e^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} + e^-$ for O₂ and N₂O, respectively. The threshold energy for dissociation will be further reduced to 3.64 eV for O₂ through an electron dissociative attachment (i.e., $e^- + \text{O}_2 \rightarrow \text{O}^- + \text{O}$).³² For N₂O, the electron-impact dissociative attachment (i.e., $e^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$) has a primary threshold energy at 2.3 eV and a nearby shoulder at 0.7 eV. Elevating the gas temperature was reported to further shift the threshold energy to lower magnitudes.^{33,34}

In addition, it was also previously pointed out that at low temperature the associative detachment of N₂O could also be relevant in eliminating O[−] ions and generating free electrons, via $\text{O}^- + \text{N}_2\text{O} \rightarrow \text{N}_2\text{O} + e^-$.³⁵ Using N₂O instead of O₂ was expected to create a more reactive environment, i.e., by generating a higher amount of atomic oxygen to react with other plasma species.^{7–24} Therefore, the N₂O was practically used as an alternative background to O₂ in oxide thin film depositions via not only PLD,^{7–14} but also sputtering^{15–17} and plasma-enhanced chemical vapor deposition (PECVD).^{18–24} Nevertheless, despite exhibiting a larger oxidation potential, the N₂O is more toxic and expensive than O₂. Hence, knowing the distinct physical and chemical characteristics of the laser induced plasma propagating in N₂O background gas, as compared to O₂ is rather important to the design of the thin film deposition strategy.

To address the above issue, we explore the distinct features in the composition of laser induced plasmas that propagates in N₂O background gas as compared to O₂. A large variety of laser induced plasmas, propagating in N₂O and O₂ background gases during PLD, were analyzed by using kinetic energy (E_K) resolved mass spectrometry and time resolved plasma imaging. In order to distinguish the origin of oxygen in the plasma species, one oxide target of La_{0.6}Sr_{0.4}MnO₃ was labeled with $\sim 52\%$ of the ¹⁸O isotope, and this enables a semi-quantitative investigation towards the plasma/background chemical reactions. The compositions of as-deposited thin film materials by using O₂ and N₂O background gases at

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comparable pressures were also compared. The present investigation provides guidance to the design of pulsed laser deposition strategies for specific oxide thin film materials, when it is necessary to use the N_2O as an alternative background.

II. EXPERIMENTAL

The plasma plumes for both mass spectroscopy analysis and thin film deposition were created by imaging a 248 nm laser beam, shaped by a rectangular mask, with a fluence of 1.8 J/cm^2 and a spot size of 1.4 mm^2 onto ceramic targets within a multifunctional ultra high vacuum (UHV) chamber. One $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ceramic target was labeled with the ^{18}O isotope by $\sim 52\%$. N_2O with the natural isotope ratio was used as background gas with pressures from 10^{-8} mbar to 1.5×10^{-1} mbar. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ thin films were grown on SrTiO_3 (001) substrates at 650°C or on Si (001) at room temperature by using the labeled target with N_2O as background gas. The thin film composition was analyzed by Rutherford backscattering (RBS), while the isotope ratio between ^{18}O and ^{16}O was obtained from elastic recoil detection analysis (ERDA).

Plasma imaging was performed using an Andor Solis USB iStar camera equipped with an acousto-optical tunable filter (AOTF, Brimrose VA210-40-65-H) within the range of 400–650 nm. The resolution is of $\sim 0.8\text{ nm}$ for the short wavelengths and up to 2.1 nm for the longer wavelengths. The gating time for each image with a specific delay time was 100 ns, and 100 frames were accumulated. To image the entire plasma (4 cm) including the target and the mass spectrometer nozzle onto the CCD, a Nikkor 28–300 mm lens

was used at a distance of 550 mm using a focal length of $\sim 200\text{ mm}$.

An electrostatic quadrupole mass spectrometer, including a high-transmission 45° sector field ion kinetic energy (E_k) analyzer, was used to analyze the relative amounts of specific plasma species with defined mass to charge ratios at specific kinetic energies. The E_k distribution of a specific species was obtained by scanning its signal as a function of its E_k . Its detected amount in total was calculated by integrating the detected amounts over the whole E_k range.

III. RESULTS AND DISCUSSION

Figure 1 shows the ionic compositions of the laser induced plasmas from the labeled $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ target material at various pressures of N_2O ($p_{\text{N}_2\text{O}}$). Similar to the results when O_2 was used as background,²⁵ enhancing the $p_{\text{N}_2\text{O}}$ shifts the oxygen isotope ratio towards the ^{16}O containing species due to reactions between the plasma species and N_2O molecules. This results in a predominant formation of positive diatomic metal-oxygen ions (MO^+). Although diatomic positive metal-nitrogen ions (MN^+) are also detected, their amounts are, in general, much smaller as compared to MO^+ . Among the negatively charged species, O^- is the most prominent species observed for all used pressures. This observation may be associated with the electron-impact dissociative attachment of the N_2O and O_2 background gases, which can significantly reduce the magnitude of the dissociation energy of the background gas molecule and forms the O^- species.^{32–34} In addition, the negative metal-oxygen ions, such as MnO^- and MnO_2^- , are also observed in the pressure range up to 10^{-2} mbar, while at the highest

FIG. 1. Mass spectra of positive and negative ionic plasma species from the laser ablated $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}^{16,18}\text{O}_3$ target (contains ^{18}O of $\sim 52\%$) at various N_2^{16}O pressures of 2×10^{-3} mbar, 1×10^{-2} mbar, and 1.5×10^{-1} mbar.

pressure of 10^{-1} mbar these species are only present in traces. These observations are similar to the previously reported ones when using O_2 as background in comparable pressure ranges.²⁵

The results shown in Fig. 1 reveal that MO^+ is a main product from the oxidation of the metallic plasma species by the N_2O background gas. Therefore, the metallic oxidation in the plasma is further evaluated by using the ratio of the positive metal oxygen ion divided by the sum of metallic and metal oxygen positive ions, as $MO^+/(M^+ + MO^+)$, similar to the way shown in Ref. 26. In Figs. 2(a) and 2(b), the $MO^+/(MO^+ + M^+)$ ratios are compared for La, Mn, and Sr, plotted as a function of the pressures of N_2O and O_2 . As shown in Fig. 2(a), the tendency in the oxidation for La and Mn when increasing the p_{N_2O} is similar to the one previously reported for p_{O_2} . For example, at a relatively high background pressure, La is effectively oxidized also due to the high chemical stability of LaO^+ (dissociation energy of ~ 8.9 eV).²⁵ In contrast, it is not possible to fully oxidize Mn via plasma reactions with the background gas molecules due to the relatively low chemical stability of MnO^+ (~ 2.9 eV).²⁵ The main difference for using N_2O instead of O_2 as a background gas is observed in the oxidation of Sr, as shown in Fig. 2(b). The data reveal that Sr can be fully oxidized at a relatively high p_{N_2O} , which is not achievable when using O_2 as background gas at comparable pressures.

The more effective oxidation of Sr when using N_2O as is also demonstrated by the time and wavelength resolved plasma imaging, at the characteristic emission wavelengths of the neutral Sr(I) at 496.2 nm, and SrO species at 400.0 nm. In Fig. 2(c), the spatial distribution of the excited Sr(I) and SrO is compared for the plasmas created by laser ablating the $La_{0.4}Sr_{0.6}MnO_3$ target in vacuum (pressure below 10^{-6} mbar) or in O_2 , N_2O , and Ar background gases at a pressure of 1×10^{-2} mbar. In vacuum, the plasma species do not encounter pronounced collisions and expand freely.^{27,28} In that case, the emission intensity of Sr(I) decreases with propagation time due to the emission life time, and as a result the SrO is not observed. At 1×10^{-2} mbar Ar, the shape of the Sr(I) plume is changed by collisions with the Ar atoms, and no SrO is observed. At 1×10^{-2} mbar O_2 and N_2O , pronounced signals of both Sr(I) and SrO are observed. Comparing the intensities for O_2 and N_2O as background gases indicates a much larger amount of SrO in N_2O background, while the intensity detected for Sr(I) exhibits the opposite tendency. This observation is in agreement with the mass spectrometry results shown previously and indicates a more effective oxidation of the Sr metallic species by interacting with the N_2O background gas molecules or interacting with the atomic oxygen formed by the collision dissociation of N_2O .

FIG. 2. Oxidation of metallic positive ions indicated by $MO^+/(M^+ + MO^+)$ for (a) La and Mn and (b) Sr as a function of the N_2O and O_2 background pressures. (c) Time resolved plasma imaging of Sr(I) (496.23 nm) and SrO (439.96 nm) in vacuum as well as 1 mbar background pressure of O_2 , N_2O , and Ar.

To further study the oxidation of the metallic species via interactions with N_2O , a large variety of metallic elements within different oxide target materials, i.e., $La_{0.6}Sr_{0.4}MnO_3$, $YBa_2Cu_3O_7$, $SrTiO_3$, $SrMoO_4$, $TbMnO_3$, $LuMnO_3$, $TmMnO_3$, and $La_{0.4}Ca_{0.6}MnO_3$, $La_{0.8}Ca_{0.2}CoO_3$, $La_{1.85}Sr_{0.15}CuO_4$, ZnO , 8-YSZ, and Al_2O_3 , was applied. In Figs. 3(a) and 3(b), we summarize their $MO^+/(M^+ + MO^+)$ ratios when performing laser ablation at 1×10^{-2} mbar and 1.5×10^{-1} mbar pN_2O . The same laser ablation conditions as for the studies in an O_2 background²⁶ were used. The distinct feature when using the N_2O background, compared to O_2 , is observed for the significantly enhanced oxidation of the alkaline-earth metallic elements, i.e., Ca, Sr, and Ba. It is noteworthy that their MO^+ dissociation energies are within the range of 3–5 eV. In that case, their chemical stabilities are in between the bond energy of N_2-O (1.6 eV) and $N \equiv NO$ (4.9 eV),³⁰ and larger than the reported most probable resonance energy between electrons and N_2O (~ 2.25 eV).³¹

In addition to the metal oxygen plasma species, the oxygen species (i.e., O^- , O , O^+ and O_2^-) are also expected to be important for the deposition kinetics as well as the oxygen content of the deposited thin films.^{25,26} Figure 4 shows the

spatial distribution of the excited oxygen species in vacuum as well as N_2O and O_2 background gases as a function of the plasma propagation time. As compared to the situation in vacuum, the intensities from excitation of ionic $O(II)$ within the plasmas in O_2 and N_2O are brighter (more species are present), due to the plasma interactions with the oxygen containing background molecules. It is interesting to note that at a background pressure of 1×10^{-2} mbar, a cone shaped and more elongated spatial distribution (i.e., normal to the target surface) of the species is observed in N_2O , in contrast to a more spherical-shaped plume as observed in O_2 . This reveals the possible turbulence in the propagation of the plasma species in 1×10^{-2} mbar N_2O , resulting in a more centralized distribution of the plasma species as compared to the situation in 1×10^{-2} mbar O_2 . This might be associated with the distinguished physical and/or chemical properties of the N_2O molecule. For example, the N_2O molecule exhibits higher dissociability and larger molecule mass and size, as compared to O_2 . During central collisions between the background gas molecules and plasma species, the easier dissociation of the N_2O background molecules reduces their interaction strengths with the plasma species. This reduces the momentum loss and the proportion of elastic scattering of the plasma species propagating along the normal direction to the target surface. In contrast, for non-central collisions where the interaction strength is not enough to dissociate the background molecules, a larger momentum loss via elastic scattering of the plasma species is expected for using N_2O compared to O_2 . By further enhancing the background pressure further to 1.5×10^{-1} mbar, smaller differences in the plasma shape are observed for the cases when using O_2 and N_2O . In this relatively high pressure range, the plasma species transfer as a shockwave,^{27,28} in which situation the re-excitations of atomic oxygen species are the most pronounced, which should be associated with the enhanced number of collisions within the shockwave-front.

Figure 5(a) shows the kinetic energy (E_K) distributions of the atomic oxygen ions (O^+ and O^-) from both the target and background when ablating the $La_{0.6}Sr_{0.4}Mn^{16,18}O_3$ in various background pressures of O_2 or N_2O . The separation of the origin of these species from background or target was described previously in Ref. 25. Briefly, the amount of a specific oxygen containing plasma species that originates from the target material (A_{Target}) is calculated from the amount of ^{18}O containing species ($A_{^{18}O}$), obtained from: $A_{Target} = A_{^{18}O}/52\%$, where 52% is the ^{18}O ratio of the target material. Therefore, the amount of the respective species originating from the background gas ($A_{Background}$) is calculated by $A_{Background} = (A_{^{18}O} + A_{^{16}O}) - A_{Target}$, where $A_{^{16}O}$ represents the amount of the specific ^{16}O containing species. The kinetic energy distributions of the directly measured $^{16}O^-$, $^{18}O^-$, $^{16}O^+$, and $^{18}O^+$ are shown in Fig. S1. At 1×10^{-2} mbar N_2O , a higher amount of O^- originating from the target with larger E_K is observed, as compared to a background of 1×10^{-2} mbar pO_2 . This observation is in agreement with our previous suggestion that the plasma species originating from the target material are less scattered via central collisions with N_2O , as compared to O_2 , before forming a shockwave. No significant differences for the oxygen species

FIG. 3. Ratio of $MO^+/(M^+ + MO^+)$ vs. dissociation energy of MO^+ species as determined at pN_2O of (a) 1×10^{-2} mbar and (b) 1.5×10^{-1} mbar, over a large variety of laser induced plasma species elements. The $MO^+/(M^+ + MO^+)$ shown for a metallic element is the average value from different oxide targets, and the error bar represents their standard deviation.

FIG. 4. Time resolved plasma imaging of OII (495.6 nm) in laser induced $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ plasmas propagating in vacuum as well as O_2 and N_2O background gases.

originating from the background for the two gases, i.e., N_2O or O_2 , at the pressure of 1×10^{-2} mbar are observed. Increasing the background pressure to 3×10^{-2} mbar and further up to 1.5×10^{-1} mbar reduces E_K of atomic oxygen ions (i.e., O^+ and O^-) and also their amount originating from the target. At all these pressures, the amount of O^- , as compared to O^+ , is larger in N_2O than in O_2 at the same nominal pressure. This observation may be associated with a more effective electron-impact dissociative attachment of the N_2O background molecules as compared to O_2 , as attributed to its smaller dissociation energy. In addition, it is also worth noticing that the kinetic energy distributions of the ionic oxygen species consist of multiple peaks, which may be caused by the different mechanisms associated with their formations. For example, the kinetic energy of the generated ionic species after plasma/background or electron/background interactions could be larger via the electron dissociative attachment of the background gas molecule, in which case the dissociation energy is reduced.

In Fig. 5(b), we further extend the mass spectroscopy investigation to the laser induced plasmas containing a large variety of materials systems at a pressure of around 10^{-1} mbar, which is the most commonly used background pressure in PLD.²⁶ For all the investigated target materials, larger amounts of O^- were observed for N_2O as background gas as compared to O_2 , while the opposite trend is observed for the amount of O^+ .

From the results shown above, we can see that the dissociable plasma species (i.e., CaO^+ , SrO^+ , and BaO^+) and electron detachable plasma species (O^-) exhibit a larger species amount for using N_2O as a background gas, as compared to O_2 . This indicates an increased potential in the generations of these dissociable or electron de-attachable plasma species over their dissociations in N_2O , compared to O_2 . This is expected to be achieved via the easier dissociation of the N_2O molecule during their central collisions with the plasma species, which reduces the interaction strength. This understanding is further supported by the larger kinetic energy of the other ionic plasma species detected at 1.5×10^{-1} mbar N_2O as compared to O_2 (see Fig. S2). In that case, a smaller interaction strength with N_2O than O_2 is also indicated by the larger momentum preserved for the plasma species after central collisions with the background molecule.

It is also worth noticing that in the present investigation, the plasma analysis was performed at room temperature. In the practical thin film deposition process, the substrate is usually heated up, and this may further results in the reduction of the local partial pressures near the substrate⁹ or slightly alter the chemical behaviors of the reactive background molecules.^{33,34} Apart from the plasma analysis approaches used in the present investigation, an additional analysis based on the use of optical emission spectroscopy techniques may also be helpful to compare the dynamic

FIG. 5. (a) Kinetic energy distribution of O^- and O^+ species originating from the target and background interactions at various pO_2 or pN_2O . (b) Comparison of the O^- and O^+ species amount when ablating various targets in 1.5×10^{-1} mbar N_2O and O_2 , with an ablation fluence of 1.8 J/cm^2 for perovskites and 2.5 J/cm^2 for other oxides.

plasma properties (i.e., electron temperature and density) in various background gases in the future investigations.^{36–39}

Finally, it is important to analyze how the variations in plasma composition and kinetic energy further influence the film composition. Figure 6(a) shows the composition of as deposited $La_aSr_bMn_cO_d$ films (no annealing in oxygen after the deposition) on STO substrates deposited at 650°C , obtained from Rutherford Backscattering (RBS), in various pN_2O as well as pO_2 . As grown thin films in N_2O are crystalline and exhibit similar XRD patterns (see Fig. S3), compared to the situation when using an oxygen background gas at similar pressures.²⁶ Comparing the cation composition in Fig. 6(a) indicates a loss of the lighter metallic elements, i.e., Sr and Mn, compared to La, observed at $\sim 10^{-2}$ mbar pN_2O (round symbol in red). This observation is similar to the

previously reported ones when performing comparable thin film depositions of $La_aSr_bMn_cO_d$ in O_2 [square symbol in black in Fig. 6(a)].²⁶ The deficiencies in the lighter cation compositions observed at 10^{-2} mbar for both N_2O and O_2 background gases were attributed to the more significant scattering of the lighter plasma species via elastic collisions with the background molecules at a transition pressure range from plasma free propagation to shockwave propagation.²⁶ For example, when the background pressure is below 10^{-2} mbar, the collision mean free path is much larger compared to the plasma propagation distance and the elastic collision frequency between the plasma species and the background molecule is low. The significant elastic scatter of the plasma species by the background molecule starts at a pressure range of $\sim 10^{-2}$ mbar, in which situation the collision mean free

FIG. 6. (a) Composition of La_{0.6}Sr_{0.4}MnO₃ thin films deposited on the (001) SrTiO₃ substrate measured as a function of the N₂O (round symbol in red) or O₂ (square symbol in black) background pressures by using Rutherford backscattering (RBS). The sum of composition of La, Sr and Mn is standardized as 2 ($a + b + c = 2$), and the composition of each element is calibrated accordingly. (b) Concentration of ¹⁸O measured by elastic recoil detection analysis (ERDA) for the La_{0.6}Sr_{0.4}MnO₃ thin films deposited in N₂O or O₂ background gases at a substrate temperature of 650 °C and room temperature (RT). (c) Proportion of the oxygen composition originates from the background gas, derived from the ¹⁸O concentration. The error to determine the composition with RBS combined with ERDA is at most 5%.

path is comparable to the plasma propagation distance. The lighter plasma species is expected to be more scattered, since their momentum will be more significantly changed upon elastic collisions. Nevertheless, when further increasing the background pressure up to the range of 10⁻¹ mbar, the way of plasma transportation will be completely altered from quasi-vacuum propagation to the shockwave propagation. In that case, the plasma species and background gas molecules were compressed within the shockwave front, resulting in effective mixing and confinement of the plasma species with various atomic weights to achieve a congruent elemental transfer from target to the substrate.²⁶

The situation for the oxygen composition for films growing at 10⁻² mbar is expected to be more complicated since there exist two competing mechanisms: (1) the preferential physical scattering will reduce the composition oxygen since it is the lightest element and (2) the chemical reactions with the oxygen containing background gas will replenish the oxygen composition. Comparing the oxygen composition of these films indicates a surprising minimum magnitude at a $p_{\text{N}_2\text{O}}$ of 10⁻² mbar range. This could be associated with a more pronounced preferential physical scattering of oxygen (reduces the content of the lighter oxygen in the films compared to the cations)^{25,26} at the transition pressure range, over the compensation of oxygen from the N₂O background (releasing only one atomic oxygen upon dissociation). In addition, the lower oxygen content in the film deposited in 1×10^{-2} mbar N₂O, where a higher amount of O⁻, SrO⁺ are detected in the plasma, suggests that, at least in this case, the observation of only these two species is not enough to fully understand and predict the oxygen content in the film. Neutral species, scattering, and reactions may influence the

oxygen content. Nevertheless, at the most commonly used deposition pressure in PLD, i.e., in the 10⁻¹ mbar range when the plasma forms a shockwave, larger oxygen contents are observed for the films grown in N₂O as compared to O₂. Although there are some metal-nitrogen plasma positive ions detected by the mass spectrometry, the ERDA results indicate a rather low nitrogen content below 0.5 at. % in the deposited film (see Table S2). Figure 6(b) shows the ¹⁸O isotope content (in percentage) of the La_{0.6}Sr_{0.4}MnO₃ films grown on SrTiO₃ substrates, in which cases the target material labeled with the ¹⁸O isotope. Since the diffusion of oxygen from the substrate to the film is not important for the depositions of La_{0.6}Sr_{0.4}MnO₃ on SrTiO₃,²⁶ the background contribution to film oxygen content can be further estimated from the oxygen isotope ratio, as shown in Fig. 6(c) vs. $p_{\text{N}_2\text{O}}$ as well as p_{O_2} . The proportion of the thin film oxygen composition originating from the background gas increases with increasing background pressure. When growing the films at 650 °C, the background gas contribution to the film oxygen content is larger for using N₂O as compared to O₂, while the oxygen content is similar for both background gases when growing the films at room temperature. This result is most likely due to the higher chemical reactivity of the N₂O molecule as compared to O₂. By elevating the substrate temperature to 650 °C, the oxygen isotope of as-grown thin films is expected to be more easily exchanged by the oxygen originating from background molecules.

IV. CONCLUSION

In conclusion, the compositions and kinetic energies of laser induced plasmas propagating in N₂O and O₂ background at various pressures are compared by two

complementary plasma analysis techniques, i.e., mass spectrometry and plasma imaging. When using N₂O as background gas, the plasma contains a larger proportion of oxygen ions with a negative charge. In addition, the alkaline-earth metallic elements can be fully oxidized when performing PLD in the N₂O background, which is not achievable for using O₂ as background gas. These distinguished chemical features are most likely associated with the lower dissociation energy of N₂O as compared to O₂, and this reduces the interaction strength during their central collisions with the plasma species and results in the easier formation of the atomic oxygen plasma species. The difference in plasma composition is expected to further influence the deposition kinetic processes, but not necessarily results in larger oxygen contents for using N₂O instead of O₂ when performing the deposition in the 10⁻² mbar pressure range. This may be related to a more pronounced preferential elastic scattering to cause the loss in the composition of the lightest oxygen transported from the target, over and the replenished oxygen composition from background gases at the pressure range of 10⁻² mbar. Nevertheless, in the most commonly used pressure range for PLD, i.e., ~10⁻¹ mbar, when the plasma propagates as a shockwave, a larger oxygen content was achieved by using N₂O as the background gas, instead of O₂. The present investigation reveals that during the PLD process, the oxygen content in the films can be improved by using N₂O as an alternative background gas to O₂, which is related to the plasma interaction with the N₂O background.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) available online showing the kinetic energy distribution of ionic plasma species from La_{0.6}Sr_{0.4}Mn^{16/18}O₃ plasmas propagating in various *p*O₂ and *p*N₂O (Figs. S1 and S2); XRD patterns (Fig. S3) and nitrogen compositions (Table S1) of La_{0.6}Sr_{0.4}MnO₃ thin films grown at various *p*N₂O.

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