Negative ions: The overlooked species in thin film growth by pulsed laser deposition

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Plasma plume species from a ceramic $La_{0.4}Ca_{0.6}MnO_3$ target were studied by plasma mass spectrometry as a function of laser fluence, background gas, and deposition pressure to understand the interplay between plasma composition and oxide thin film growth by pulsed laser deposition. The plume composition reveals a significant contribution of up to 24% of negative ions, most notably using a N_2O background. The significance of negative ions for thin film growth is shown for $La_{0.4}Ca_{0.6}MnO_3$ films grown in different background conditions where the best structural properties coincide with the largest amount of negative plasma species. © *2011 American Institute of Physics*. [doi:10.1063/1.3660399]

One of the most versatile deposition techniques in solid state physics and analytical chemistry is the vaporization of condensed matter using photons. For oxide thin film growth, pulsed laser deposition (PLD) has evolved into a powerful deposition technique with a high control over crystalline properties.[1,2] Material removed from the target is directed towards a substrate where it re-condenses to form a film. The film's growth kinetics will depend on the material flux, plume composition, laser repetition rate, growth temperature, substrate, pressure, and background gas (vacuum, reactive). In addition, wavelength and fluence will determine if thermal or non-thermal evaporation processes are dominant as well as control the ratio between neutral and ionized species in a plume.[3]

An important characteristic of PLD is the ability to realize, in principle, a stoichiometric transfer of ablated material from multi-elemental targets. This is an interesting fact, often taken for granted[2–5] but not necessarily correct in general.[6] However, the question is which plasma conditions have to be realized in order to grow a stoichiometric thin film with good properties, e.g., crystallinity. The ablation and deposition processes are connected by the transfer of material via the created plasma plume, and the thin film properties are closely related to the dynamics and composition of the respective plasma plume and growth properties on a substrate. To enhance the oxygen content in oxide thin films, a background gas is introduced, which also helps to moderate the kinetic energy (KE) of plume species.[1]

Which plasma species are important for thin film growth? For sputtering, plasma species have been studied in detail, including the influence of negative ions. A densification of a film in the initial stages by ion bombardment has been linked to the presence of negative ions.[7] Likewise, negative ions are involved in an increase of the adatom's mobility which is a function of adatom to ion ratio. This is of particular importance for the kinetic energies of plasma species as low as 2–18 eV (Ref. 8) and typical when a background pressure is applied during film growth. The result is an increased nucleation density of up to $10^9\,cm^{-2}$. It is noteworthy to point out that negative oxygen ions are the more active oxidizing species compared to O^+ as shown for silicon oxidation.[9]

The example of the sputter plasma composition shows the positive influence of negative ions for thin film growth and properties. For PLD, positive ions are typically considered to be the more relevant species,[10,11] and the role of negative ions for the growth of thin films has not been widely investigated, yet.[12–14] In Ref. 12, the authors noted an increase in negative species in the plasma when introducing N_2O using a synchronized gas pulse and speculated on the link between plasma composition and film growth. To probe plasma properties including composition and correlate it with structural film properties, an ArF excimer laser ($\lambda = 193$ nm, $\tau = 20$ ns, 10 Hz) was used for plasma analysis and thin film growth, as this wavelength provides the largest photon energy (6.4 eV) of all commonly used excimer lasers. The dissociation energy for LaO (8.2 eV), MnO (4.13 eV), and CaO (4.11 eV) compared to 6.4 eV for $\lambda = 193$ nm should give indications about the origin of the molecule, e.g., target or plasma. The beam was imaged with an optimized laser fluence $F = 1.5\,J\,cm^{-2}$ (spot size: 1.4 mm^2) onto a rotating ceramic $La_{0.4}Ca_{0.6}MnO_3$ (LCMO) target in a vacuum chamber (base pressure $< 6 \times 10^{-9}$ Pa) with different background conditions (vacuum, N_2O, and O_2 from 2×10^{-5} to 1.5×10^{-1} Pa). N_2O as background gas is introduced because it should result in the highest amount of oxygen in the as-grown film. LCMO Films were grown on TiO_2-terminated $SrTiO_3$ substrates[15] at a growth temperature, $T_S = 750\,°C$, and a target-to-substrate distance of 4 cm. After the deposition, the films were cooled down to room temperature in vacuum. To investigate the plasma, an electrostatic quadrupole plasma analyzer, consisting of a high-transmission 45° sector field ion energy analyzer and a quadrupole mass spectrometer (QMS, Hiden), was placed perpendicular to the target at a distance of 4 cm.

The parameter set of $F = 1.5\,J\,cm^{-2}$ and $p_{N_2O} = 1.5 \times 10^{-1}$ Pa at $T_S = 750\,°C$ results in LCMO thin films grown on (100) $SrTiO_3$ with excellent crystalline properties compared to LCMO films prepared in an oxygen background

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and vacuum. The LCMO film compositions as analyzed by Rutherford backscattering (RBS) are $La_{0.44}Ca_{0.56}Mn_{0.95}O_{2.40}$, $La_{0.41}Ca_{0.59}Mn_{0.95}O_{2.55}$, and $La_{0.39}Ca_{0.61}Mn_1O_{2.75}$ for vacuum, O_2, and N_2O depositions, respectively, and are in good agreement with the target cation composition.[16] An oxygen content smaller than $x = 3.0$ is also reasonable due to the film preparation without additional oxygen treatment[17] with the oxidizing environment (O_2, N_2O) providing significantly more oxygen to the as-grown film as verified by RBS. Films grown in vacuum are (100)-oriented and almost strain free with a very broad rocking curve (FWHM $> 2°$) (see Fig. 1). Films grown using a background gas are single phase, (001)-oriented with a tensile strain $>2\%$. The FWHM of the rocking curves are 0.15° and $<0.07°$ for films grown in O_2 and N_2O, respectively. Both values are considered to be indicative of a good to already excellent crystalline quality for the as-grown (001) oriented films. Remarkable is the change from a (100) to a (001) growth orientations and the sharpening of the FWHM of the corresponding rocking curves depending on the background conditions for the same laser fluence (see Fig. 1). A change in crystallinity and crystalline orientation can be attributed to larger kinetic energies of plasma species in vacuum as compared to species in a background gas affecting the growth kinetics of the respective films.[1]

The laser induced plasma consists of ionic (positive and negative) and neutral species. Figure 2(a) shows a mass spectrum of all negative species measured ($p_{N_2O} = 1.5 \times 10^{-1}$ Pa). The intensity for O is the largest and more than twice the amount measured for O^+ (not shown).[16] In addition, the presence of oxide species like MnO^- or CaO^- is very pronounced and complemented by a strong presence of di- and tri-oxy species, e.g., MnO_2^- or MnO_3^-. This is in contrast to the measured positive or neutral species, where more elemental and diatomic species are found, larger oxygen-containing fragments are scarce. Overall, the presence of O_2 and N_2O enhances the number of Ca and Mn diatomic species significantly. Quantifying all species for a N_2O background, the total yield is 24%, 36%, and 40% for negative, positive, and neutral species, respectively, in O_2 12%, 55%, and 33%, and in vacuum 14%, 50%, and 36%. Please note, the data have not been corrected for the detection efficiency (ions ~100%, neutrals depend on the specific ionization efficiency of each species, which is unknown for our experiments[16]). With this in mind, evaluating just the total intensity of the ionic species, a doubling of negative species produced in N_2O with respect to vacuum or O_2, where the numbers are comparable, is significant.

KE measurements for the most prominent plasma species, LaO^+, representative for the majority of ionic plasma species, with respect to background conditions is shown in

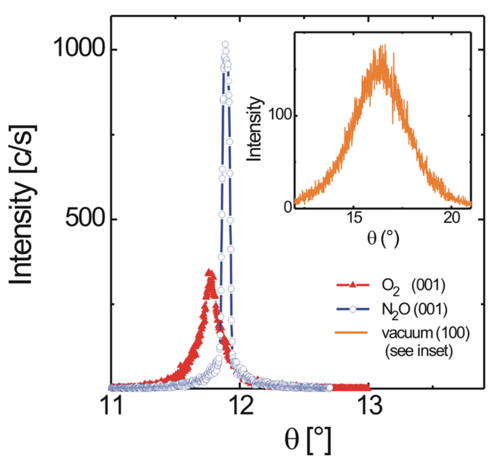

FIG. 1. (Color online) Rocking curves of the (100) (inset) and (001) film peaks for LCMO films grown at $T_S = 750\,°C$ with a fluence of $1.5\,J\,cm^{-2}$ and 193 nm irradiation in vacuum (inset), and a O_2 and N_2O background pressure of 1.5×10^{-1} Pa.

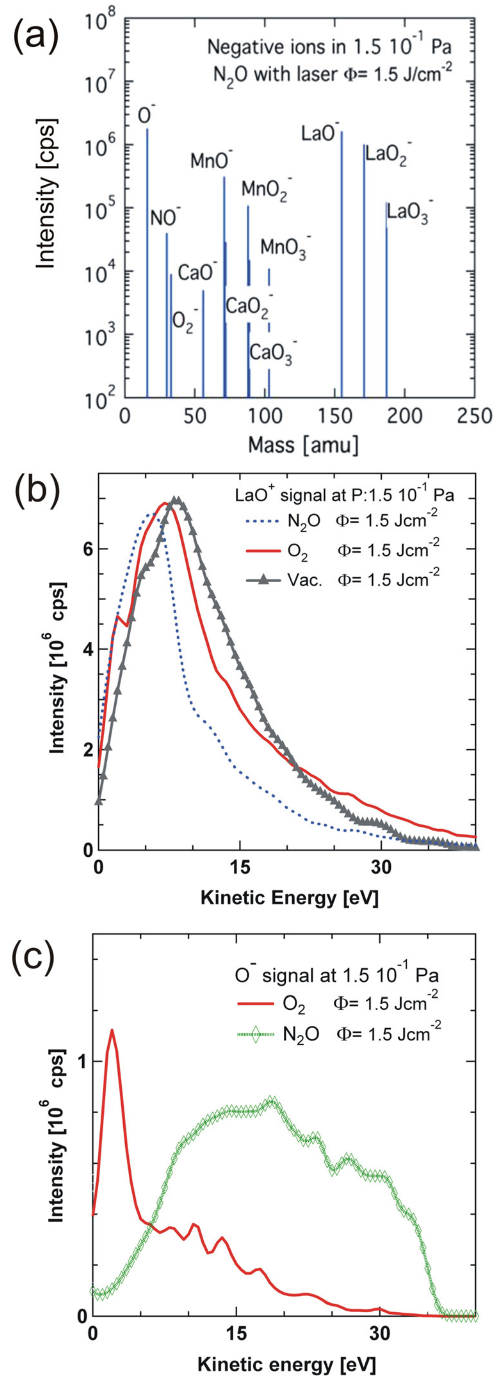

FIG. 2. (Color online) (a) Mass spectrum of negative ions for a $La_{0.4}Ca_{0.6}MnO_3$ ablation plasma using a 193 nm ArF laser at a N_2O pressure of 1.5×10^{-1} Pa and a fluence of $1.5\,J\,cm^{-2}$. Kinetic energy distributions for (b) LaO^+ in vacuum, O_2, and N_2O, and (c) O^- species at 1.5 Jcm^{-2} in O_2 and N_2O.

TABLE I. Most probable kinetic energies (eV) of ablated species from a $La_{0.4}Ca_{0.6}MnO_3$ target as measured from the kinetic energy distributions at different background conditions. The used laser fluence was 1.5 J cm^{-2} and 193 nm irradiation.

Environment/species	Vacuum	O_2	N_2O
La	12	10.5	8
La^+	8.5	7.5	7
LaO	11	—	2
LaO^+	8	6.5	5.5
LaO^-	0.5	4.5	4.5
Ca	16	14	14
Ca^+	5.5	3.5	2
CaO^+	—	3	2
CaO^-	—	2.5	0.5
Mn	22.5	20.5	17
Mn^+	8	5.5	5
MnO^+	—	3	1.5
MnO^-	5.5	2.5	0.5
O	3.5	3	2
O^-	0.5	2	8-34

Fig. 2(b). The KE distribution can be described using a single Maxwell-Boltzmann (MB) function (vacuum) or a linear combination with different peak kinetic energy values (O_2, N_2O). From these measurements, the maximum KE for different species is extracted and summarized in Table I. For LaO^+, a reduction of the KE is observed depending on the background, whereas the total signal remains almost unchanged indicating that most of the measured LaO^+ originates from the target. The KE distribution for O^- species in O_2 can be approximated by a MB distribution, whereas O^- in N_2O for the same fluence is best described by a broad KE distribution with KE ranging from 8–34 eV (Fig. 2(c)). Unlike the KE distribution in O_2, the broad kinetic energy spectrum seems to be a direct result of a dissociation of N_2O into N_2 and atomic oxygen which also coincides with a significant increase of negative ions in the plasma. The presence of these ions, in particular, the amount of O^-, can be explained by an electron attachment process which becomes more pronounced in a N_2O background due to the creation of atomic oxygen.[18,19] The enhanced presence of O^- combined with the broad KE distributions, therefore, leads to a measurable increase in the total yield of negative ions in the plasma, in particular, negative metal-oxide species. In addition as shown in Table I, the maximum KE is background and species dependent with the following relationship: neutral metals typically have the largest KEs and positive ions have a larger KE than negative ions. All species with the exception of O^- are slowed down in background, most efficiently in N_2O. A reduced kinetic energy is usually considered to be beneficial for oxide film growth leading to good crystalline properties.[1] Incidentally, the best crystallinity for the thin film growth is achieved by the nominally most oxidizing growth conditions and overall smallest kinetic energies of oxygen containing species. This includes the large KE of O^- which seems, contrary to expectations, not harmful for the oxide thin film growth. In addition, the deposition of LCMO in N_2O also improves the oxygen content of the film as measured using RBS. The combined findings of the plasma composition, stoichiometry, and structural data lead to the conclusion that negative ions are fundamental for the growth of metal-oxide thin film using PLD, and their influence on oxide thin film growth has been underestimated.

In conclusion, the ablation plasma plume properties of LCMO as a function of laser fluence and background conditions were investigated, and epitaxial, stoichiometric thin films have been prepared on (100) $SrTiO_3$ substrates. It was demonstrated that the quantified plume composition reveals a significant contribution of up to 24% of negative ions in addition to the expected positive and neutral species, in particular, if N_2O as background gas is used. Combing plasma, structural, and compositional information, it is concluded that negative species, in particular, O^- in a laser induced plasma, are very supportive to grow high quality oxide thin film, and the value of negative ions for PLD oxide thin film growth has been underestimated. These findings are also expected to hold for a laser wavelength of 248 nm.

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[1]D. B. Chrisey and J. R. Huber, *Pulsed Laser Deposition of Thin Films* (John Wiley & Sons, Inc., New York, 1994).
[2]C. W. Schneider and T. Lippert, in *Springer Series in Material Science*, edited by P. Schaaf (Springer, Berlin, 2010), Vol. 139, pp. 89–112.
[3]W. Kautek, B. Roas, and L. Schultz, Thin Solid Films **191**(2), 317 (1990).
[4]P. R. Willmott and J. R. Huber, Rev. Mod. Phys. **72**(1), 315 (2000).
[5]R. Eason, *Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials* (Wiley, Hoboken, 2008).
[6]S. Canulescu, E. L. Papadopoulou, D. Anglos, T. Lippert, C. W. Schneider, and A. Wokaun, J. Appl. Phys. **105**(6), 063107 (2009).
[7]K. Teii and T. Yoshida, J. Appl. Phys. **85**(3), 1864 (1999).
[8]K. Teii, M. Hori, and T. Goto, J. Appl. Phys. **89**(9), 4714 (2001).
[9]T. Koromogawa, T. Fujii, A. Yamashita, Y. Horiike, and H. Shindo, Jpn. J. Appl. Phys., Part 1 **37**(9A), 5028 (1998).
[10]N. V. Joshy and M. K. Jayaraj, J. Phys.: Conf. Ser. **208**(1), 012131 (2010).
[11]H. S. Kwok, Thin Solid Films **218**(1–2), 277 (1992).
[12]S. Canulescu, T. Lippert, and A. Wokaun, Appl. Phys. A **93**(3), 771 (2008).
[13]S. C. Langford, L. C. Jensen, J. T. Dickinson, and L. R. Pederson, J. Appl. Phys. **68**(8), 4253 (1990).
[14]S. R. George, S. C. Langford, and J. T. Dickinson, J. Appl. Phys. **107**(3), 033109 (2010).
[15]M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, Science **266**(5190), 1540 (1994).
[16]M. Esposito, "Thin metall oxide films by PLD: 'Tracing' the oxygen and understanding its role," Ph.D. thesis (ETH Zürich, 2011).
[17]C. W. Schneider, M. Esposito, I. Marozau, K. Conder, M. Doebeli, Y. Hu, M. Mallepell, A. Wokaun, and T. Lippert, Appl. Phys. Lett. **97**(19), 1921073 (2010).
[18]S. Amoruso, C. Aruta, R. Bruzzese, D. Maccariello, L. Maritato, F. M. Granozio, P. Orgiani, U. S. di Uccio, and X. Wang, J. Appl. Phys. **108**(4), 043302 (2010).
[19]C. Aruta, S. Amoruso, R. Bruzzese, X. Wang, D. Maccariello, F. M. Granozio, and U. S. di Uccio, Appl. Phys. Lett. **97**(25), 252105 (2010).