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Ion concentrations in plasmas produced from 193 nm excimer laser irradiation of LiNbO₃ in vacuum and gas atmospheres

F. J. Gordillo-Vázquez^{a)} and J. Gonzalo

Instituto de Óptica, CSIC, Serrano 121, 28006 Madrid, Spain

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We have calculated the concentration of ions in the plasma produced upon ablation of LiNbO₃ with a low fluence ArF excimer laser in vacuum and different gas environments (Ar and O₂). The model shows that Li and Nb ions (with the amount of Li ions being greater than that of Nb ions) are the most abundant in the plasma with their concentrations being always above their corresponding neutral densities. In addition, we show that the concentration of excited Nb ions is relatively important while no excited Li ions are predicted. We found that the concentration of both Li and Nb ions in O₂ is slightly higher than in Ar and vacuum. Moreover, the calculated spatial evolution of the ionic species suggests that a significant fraction of the predicted ion concentration is not produced by electron-atom ionization events within the plasma; on the contrary, they might have been produced in the LiNbO₃ crystal through a nonthermal mechanism and then ejected from the target after the laser pulse. © 2003 American Institute of Physics. [DOI: 10.1063/1.1628383]

I. INTRODUCTION

Pulsed laser deposition (PLD) has become a very promising tool for both advanced micromachining and high quality thin film deposition for different technological applications.¹ However, in many cases, the underlying microscopic plasma processes leading to high quality films remain obscure. In particular, the growth of good quality LiNbO₃ thin films by PLD has not been achieved in vacuum starting from a crystalline target. Instead, gas mixtures at 0.4 Torr of Ar and 0.1 Torr of O₂² or pure atmospheres of Ar or O₂ at approximately 1 Torr are needed to obtain stoichiometric films of good crystallographic quality.³ In this regard, it is important to determine the species (electrons, neutrals, and ions) concentration in the plasma together with their corresponding kinetic energy distributions. In particular, the film growth process benefits from a number of effects caused by the plasma ions such as, for instance, their positive influence on the degree of crystallographic orientation, composition, and grain size of polycrystalline films.⁴ On the contrary, self-sputtering caused by energetic ions can lead to nonstoichiometric films.⁴

In order to investigate the role played by the plasma ions in connection with the deposition of thin films by PLD, a number of investigations have been undertaken. In this regard, Schou and co-workers^{5–9} have performed different experimental works to clarify the dynamics of the ions ejected upon laser ablation of metals together with their corresponding energy distributions. However, the works dealing with the study of the ions formed during ultraviolet (UV) laser ablation of wide band gap dielectric materials are much more scarce.^{10,11}

In the present work, we have used an analytic approach to quantify the concentrations of neutrals and, especially, of

ions present in the plasma formed after irradiating a relatively wide band gap (~ 4 eV) dielectric material such as LiNbO₃ with an ArF excimer laser (photon energy = 6.4 eV) working at a relatively low fluence of 1.2 J cm^{-2} and an angle of incidence of 45° . The latter fluence and angle of incidence are chosen because they are the ones typically used to grow good quality LiNbO₃ films for which, in addition, we have previously measured^{12,13} the values of the electron density and electron temperature used as input parameters of the present model. The approach chosen here is based on previous results indicating the existence of local thermodynamic equilibrium (LTE) in the laser-produced plasma under the conditions of interest for the deposition of LiNbO₃ films.^{12–15}

The present model predicts that the ion concentration in the plasma is always several times greater (up to 60 and 20 times, respectively, for Li and Nb ions in vacuum) than their corresponding concentration of neutrals. This result is important since ions are generally more energetic than neutrals and, consequently, can have a deeper influence on the thin film growth process. Close to the substrate where the film growth takes place, the model predicts a slightly higher Li ion concentration (especially in O₂) than that of Nb ions. However, the concentration of Nb neutrals is always greater (by about four times) than that of Li neutral atoms. When considering different gas environments, the concentration of neutrals is highest in O₂, followed by Ar and vacuum. Finally, we have also predicted that the concentration of excited Nb ions in the laser produced plasma is relatively important and that the total ionization degree of the plasma is quite high, reaching values of almost 0.3 near the target.

The fact that the concentrations of ions are considerably higher than those of neutrals suggests that, as has been proposed by Dickinson and co-workers^{10,11} for the case of MgO, the UV laser light might induce an important emission yield of photoelectronic ions and electrons due to the probable

^{a)} Author to whom correspondence should be addressed; electronic mail: vazquez@io.cfmac.csic.es

presence of defects in the LiNbO₃ crystal. In addition, due to the low ionization potential (5.4 eV) of Li atoms, the UV radiation used can directly photoionize Li atoms in the solid. After the laser pulse, the Li ions would be ejected according to an electrostatic mechanism similar to the one proposed by Dickinson *et al.*¹⁶

According to the above described picture for LiNbO₃ ablation, the fact that stoichiometric films can be synthesized by PLD in Ar or O₂ atmospheres at 1 Torr rather than in vacuum might be connected to the more abundant Nb, Li, and O neutral atoms in O₂ and Ar close to the target. In addition, the presence of a higher concentration of Li ions in O₂ might contribute to the deterioration of the crystallographic quality of the films obtained in O₂ compared to those synthesised under Ar.³

Finally, we also have to consider that, in vacuum and low pressures (0.01 Torr), the lighter species (Li and O) are lost due to their broader angular distributions with respect to the heavier ones (Nb).¹⁷ However, when gas environments (at pressures of ≈ 1 Torr) are used, light species are redirected towards the center line (between target and substrate) of the plasma due to collisions with the surrounding gas.¹⁸ Therefore, in spite of the fact that the predicted concentrations of Li and Nb ions are similar in vacuum and gas, more Li and Nb ions would reach the growing film within O₂ and Ar due to the above mentioned scattering process.

II. APPROACH

Previous kinetic studies of the plasma formed after the laser ablation of LiNbO₃ crystals show that the measured electron densities are high enough ($\sim 10^{16} \text{ cm}^{-3}$) to keep LTE.¹⁴ These calculations showed that the possible nonequilibrium caused by radiation losses (assuming an optically thin plasma) is minimum since the excited Li atoms concentrations were quite close to their corresponding Boltzmann (equilibrium) distributions.¹⁴ Taking this into account, we have considered the Saha relationship between the plasma electrons and the different ionic and neutral species of the plasma together with two more equations accounting for, respectively, the macroscopic electrical quasineutrality of the plasma and the congruent laser ablation of the LiNbO₃ target.

We can assume that the highest ion concentrations in the plasma correspond to Li⁺ and Nb⁺ because: (i) The presence of LiO molecules, with a relatively low ionization potential of 8.4 eV, within O₂ atmospheres is not expected since their formation implies an endothermic reaction of Li with O₂.¹⁹ (ii) The ionization energies of Li (5.39 eV) and Nb (6.88 eV) are the lowest ones among the expected species: O (13.6 eV), O₂ (12.07 eV), and NbO (~ 10 eV). Thus, our equations can be written as

$$\frac{N_{\text{Li}}^+}{N_{\text{Li}}} = A = \frac{2Z_e Z_{\text{Li}}^+}{N_e Z_{\text{Li}}} e^{-\epsilon_i^{\text{Li}}/kT_e}, \quad (1)$$

and

$$\frac{N_{\text{Nb}}^+}{N_{\text{Nb}}} = B = \frac{2Z_e Z_{\text{Nb}}^+}{N_e Z_{\text{Nb}}} e^{-\epsilon_i^{\text{Nb}}/kT_e}, \quad (2)$$

where N_e is the electron density, and $N_{\text{Li,Nb}}$ and $N_{\text{Li,Nb}}^+$ are the total (ground and excited) number density of, respectively, Li and Nb neutrals and ions in the plasma. Moreover, Z_e , $Z_{\text{Li,Nb}}$, and $Z_{\text{Li,Nb}}^+$ are, respectively, the translational electronic partition function and the atomic (Li and Nb) and ionic (Li⁺ and Nb⁺) electronic partition functions. Finally, $\epsilon_i^{\text{Li,Nb}}$ are the ionization energies of Li and Nb atoms in their ground state and T_e is the electron temperature. We have disregarded the lowering of the ionization potentials in Eqs. (1) and (2) because their expressions in the Debye approach lead to very small values (around 0.05 eV) for the measured N_e and T_e used as input data.^{12,13} It is important to note that the plasma parameters N_e and T_e , which have been used for the present work, are time integrated so that the calculated atomic and ionic densities represent a “kind” of time average.

The equation stating the electrical quasineutrality of the plasma is

$$N_{\text{Li}}^+ + N_{\text{Nb}}^+ = N^+ \cong N_e. \quad (3)$$

Finally, the expression considering the congruent laser ablation of the LiNbO₃ crystal states that

$$3N_{\text{Li}}^{\text{TOTAL}} = 3N_{\text{Nb}}^{\text{TOTAL}} = N_{\text{O}}^{\text{TOTAL}}, \quad (4)$$

where

$$\begin{aligned} N_{\text{Li}}^{\text{TOTAL}} &= N_{\text{Li}}^+ + N_{\text{Li}}, \\ N_{\text{Nb}}^{\text{TOTAL}} &= N_{\text{Nb}}^+ + N_{\text{Nb}}, \\ N_{\text{O}}^{\text{TOTAL}} &\cong N_{\text{O}}. \end{aligned} \quad (5)$$

Since both N_e and T_e are known spectroscopic data previously measured in vacuum and Ar and O₂,^{12,13} we have the following solutions to expressions (1)–(5):

$$\begin{aligned} N_{\text{Nb}} &= \frac{N_e(A+1)}{(A+1)B + A(B+1)}, \\ N_{\text{Nb}}^+ &= BN_{\text{Nb}}, \\ N_{\text{Nb}}^{\text{TOTAL}} &= N_{\text{Nb}}(B+1), \end{aligned} \quad (6)$$

and

$$\begin{aligned} N_{\text{Li}} &= \frac{N_e - BN_{\text{Nb}}}{A}, \\ N_{\text{Li}}^+ &= AN_{\text{Li}}, \\ N_{\text{Li}}^{\text{TOTAL}} &= N_{\text{Li}}(A+1), \end{aligned} \quad (7)$$

with the total amount of ejected oxygen (without considering the oxygen coming from the O₂ atmosphere) being given by: $N_{\text{O}}^{\text{TOTAL}} = 3 \times N_{\text{Li}}^{\text{TOTAL}}$.

Once we have obtained the total amount of ions (N_{Li}^+ and N_{Nb}^+) we can derive the number densities of Li and Nb ions excited to level i , that is, $N_{\text{Li}(i)}^+$ and $N_{\text{Nb}(i)}^+$, through the well known Boltzmann relationship

$$N_{\text{Li}(i),\text{Nb}(i)}^+ = \frac{N_{\text{Li,Nb}}^+ \times g_i^{\text{Li}^+, \text{Nb}^+}}{Z_{\text{Li,Nb}}^+} e^{-\epsilon_i^{\text{Li}^+, \text{Nb}^+}/kT_e}, \quad (8)$$

where $\epsilon_i^{\text{Li}+(i),\text{Nb}+(i)}$ and $g_i^{\text{Li}+(i),\text{Nb}+(i)}$ state for, respectively, the excitation energy and the degeneracy of the corresponding excited state i of the ions considered. In general, only the concentrations of excited Nb ions are of some importance since the lowest excited level of Li^+ is roughly 62 eV above the ground ionic state.²⁰

Finally, we define the partial ionization degrees of Li and Nb, ρ_{Li} , ρ_{Nb} , and the total ionization degree of the plasma, ρ^{TOTAL} , as

$$\rho_{\text{Li}} = \frac{N_{\text{Li}}^+}{N_{\text{Li}}^+ + N_{\text{Li}}}, \quad \rho_{\text{Nb}} = \frac{N_{\text{Nb}}^+}{N_{\text{Nb}}^+ + N_{\text{Nb}}}, \quad (9)$$

and

$$\rho^{\text{TOTAL}} = \frac{N^+}{N^+ + N_e + N_{\text{Li}} + N_{\text{Nb}} + N_{\text{O}}}. \quad (10)$$

The spectroscopic constants needed to evaluate the partition functions are obtained from the Kurucz atomic line database maintained by the Harvard-Smithsonian Center for Astrophysics.²¹ We should also add that in order to have an accurate evaluation of the atomic and ionic electronic partition functions of Li and Li^+ , we only needed to consider five and one (the ground level) energy levels, respectively. However, for evaluating the atomic and ionic electronic partition functions of Nb and Nb^+ we have considered 54 and 128 energy levels, respectively.

It is important to note that the Saha equations (1) and (2) are simply a limit case of a more general expression for the ratio between the concentration of a singly ionized ion (N_a^+) and that of the corresponding neutral atom (N_a) given by²²

$$\frac{N_a^+}{N_a} = \frac{S_{1c}^a}{N_e \beta_{c1}^a + \eta_{c1} A_{c1}^a}, \quad (11)$$

where S_{1c}^a is an electron-impact ionization rate coefficient, and β_{c1}^a and A_{c1}^a are the three body collisional recombination and the radiative recombination rate coefficients, respectively. The quantity η_{c1} is a radiation escape factor accounting for the amount of radiation that leaves the plasma as a consequence of radiative recombination events. In our laser-produced plasma, we have that $N_e \times \beta_{c1}^a \gg \eta_{c1} \times A_{c1}^a$, that is, the Saha limit dominates over the corona limit. The latter is true even assuming $\eta_{c1} = 1$, that is, when maximum departure from equilibrium could be caused due to radiation escape. Thus, the three body collisional recombination exceeds radiative recombination because, for the measured N_e and T_e in our plasma, the condition $N_e > 3.1 \times 10^{13} \times T_e \text{ (eV)}^{3.75} \text{ cm}^{-3}$ for such a dominance is fulfilled (although the latter criterion is only rigorously true for hydrogenlike ions).²³

III. RESULTS AND DISCUSSION

The present model predicts how the spatial evolution of the concentrations of Li and Nb ions can be greater [see Figs. 1(a) and 1(b)] by up to 1 order of magnitude than the concentrations of neutral atoms of Li and Nb. Moreover, the amount of Li and Nb ions is higher in O_2 environments than in Ar and vacuum. Close to the substrate where the thin film

FIG. 1. Concentrations of: (a) Li and (b) Nb species both for neutrals in 1 Torr O_2 ($\blacktriangle$), 1 Torr Ar ($\bullet$), and vacuum ($\blacksquare$), and ions in 1 Torr O_2 ($\triangle$), 1 Torr Ar ($\circ$), and vacuum ($\square$). The lines are a guide for the eye.

grows, the amount of Li ions is slightly higher than that of Nb ions but, on the contrary, the concentration of Nb neutral atoms exceeds that of Li neutrals independently of the gas environment. In addition, more neutrals are predicted in O_2 than in Ar and vacuum.

It is interesting to note that, as can be seen in Fig. 2, the relative concentrations of ions with respect to neutrals of the same kind are always above one. In fact, in vacuum, these ratios can reach values of up to 60 and 20 near the ablated target for the cases of Li and Nb, respectively. In contrast, when the laser ablation process takes place in 1 Torr of O_2 or Ar, the calculated ion to neutral ratio reduces to almost half its vacuum value in the neighborhood of the target. The high density of ions obtained during the laser ablation of LiNbO_3 for which N_e and T_e (the input data of the present calculations) were measured^{12,13} can be tentatively explained in terms of different mechanisms: (i) direct photoionization of neutrals either emitted or in the solid, both mechanisms being possible in the case of Li since the energy of the laser photons exceeds the ionization energy of Li atoms; (ii) electron-impact ionization of Li and Nb atoms in the plasma; and (iii) an important photoemission yield of ions and electrons is expected (due to the presence of defects) upon absorption of UV radiation of some wide band gap

FIG. 2. Relative concentrations N_{Li^+}/N_{Li} in 1 Torr O₂ (▲), 1 Torr Ar (●), and vacuum (■), and N_{Nb^+}/N_{Nb} in 1 Torr O₂ (△), 1 Torr Ar (○), and vacuum (□) as a function of the distance to target. The lines are a guide for the eye.

dielectrics.^{10,11} In connection with the latter mechanism, Dickinson and co-workers have observed intense emission of Mg ions upon low fluence UV (248 nm) irradiation of MgO targets.^{10,11} However, this behavior does not seem to be shared by all kinds of wide band gap dielectrics since (also using 248 nm) it fails in, for instance, the case of NaNO₃.²⁴ In our case, the short wavelength used (193 nm) could enhance the laser light absorption by LiNbO₃ since the absorption coefficient in solids is proportional to λ^{-1} . In spite of this, no experimental research has been done in order to clarify the photoemission yield of ions from UV ablated LiNbO₃ crystals.

In Fig. 3 we show the concentrations of excited Nb ions corresponding to two distant energy levels. The highest density ($\sim 10^{15} \text{ cm}^{-3}$) corresponds to scarcely excited Nb ions ~ 0.099 eV above ground while the lower concentration ($\sim 10^{12} \text{ cm}^{-3}$) is the one of highly excited Nb ions ~ 5.029 eV above ground. The presence of the latter highly excited

FIG. 3. Concentration of excited Nb ions in the plasma as a function of the distance to target in vacuum (■), 1 Torr O₂ (▲), and 1 Torr Ar (●). The labels (1) and (2) correspond, respectively, to Nb ions excited to the energy levels $\epsilon_1 = 0.099$ eV and $\epsilon_2 = 5.029$ eV. The lines are a guide for the eye.

FIG. 4. (a) Total ionization degree of the laser produced plasma in 1 Torr O₂ (▲), 1 Torr Ar (●), and vacuum (■); and (b) partial ionization degrees of Li in 1 Torr O₂ (▲), 1 Torr Ar (●), and vacuum (■), and Nb in 1 Torr O₂ (△), 1 Torr Ar (○), and vacuum (□) as a function of the distance to target. The lines are a guide for the eye.

Nb ions was detected by optical emission spectroscopy (OES) since the emission transition between levels 5.029 and 2.4413 eV of excited Nb ions corresponding to 478.9 nm was used in previous works to measure T_e .^{12,13} In spite of this, only a few transitions from excited Nb ions could be clearly identified detected by OES. Thus, these highly excited Nb ions can also radiatively decay upon arrival to the growing LiNbO₃ film affecting its quality in a not yet completely explored way. According to Fig. 3, the concentration of excited Nb ions seems to be similar within vacuum and gas. Finally, we must note that excited Li ions are not predicted in our plasma since the first excited level of a singly ionized Li ion is approximately 62 eV above ground.

An important feature of plasmas is its ionization degree. In Figs. 4(a) and 4(b) we show the total ionization degree of our laser-produced plasma together with the partial ionization degrees of Li and Nb. We found that the laser-produced plasma exhibits the highest total ionization degree when laser ablation is performed in vacuum. Moreover, while it remains practically constant in vacuum (0.28–0.27) and Ar (0.26), it decreases slightly from 0.27 to 0.24 in O₂. However, what in our opinion is more interesting is that, accord-

FIG. 5. Relative concentrations (a) $N_{Li^+}^{Ar, O_2} / N_e$ in 1 Torr O_2 ($\blacktriangle$), 1 Torr Ar ($\bullet$), and vacuum ($\blacksquare$); and (b) $N_{Nb^+}^{Ar, O_2} / N_e$ in 1 Torr O_2 ($\blacktriangle$), 1 Torr Ar ($\bullet$), and vacuum ($\blacksquare$) as a function of the distance to target. The lines are a guide for the eye.

ing to Fig. 4(b), Li atoms are almost completely (singly) ionized ($0.92 \leq \rho_{Li} \leq 0.97$) independently of the gas environment. The partial ionization degree of Nb atoms is also quite high, although it varies in a wider interval ($0.65 \leq \rho_{Nb} \leq 0.95$) than ρ_{Li} . In any case, the relatively low average electron energies (0.65–0.8 eV) measured in these plasmas,^{12,13} together with our present results indicating a fewer number of Li and Nb neutrals than ions, suggest that an important part of the predicted ion concentration is not produced by electron–atom ionization events within the plasma. On the contrary, many plasma ions might have been produced (through a nonthermal mechanism) in the $LiNbO_3$ crystal being ejected further on. This result can also be partially deduced from the fact that whereas the spatial concentrations of excited Li and Nb atoms reach their maximum values a few millimeters away from the target (indicating electron–impact excitation),^{14,25} the concentration of ions is already maximum [see Figs. 1(a) and 1(b)] right at the target position either in vacuum, O_2 or Ar. Thus, a high partial ionization degree in low fluence laser-produced plasmas used for PLD of dielectrics could be considered as a distinct sign for an electronic rather than thermal ejection mechanism.

In Figs. 5(a) and 5(b) we see the predicted relative pro-

FIG. 6. Relative (a) $Li(N_{Li^+}^R)$ and (b) $Nb(N_{Nb^+}^R)$ ion concentrations in the different gas environments considered in the present work: 1 Torr O_2 to vacuum ($\blacktriangle$), 1 Torr Ar to vacuum ($\bullet$), and 1 Torr Ar to 1 Torr O_2 ($\blacksquare$). The lines are a guide for the eye.

portion of Li and Nb ions to electrons in the plasma. Roughly speaking, whereas the maximum plasma positive charge due to Li ions is 60% (in O_2), the one corresponding to Nb ions is below 50% (in vacuum).

A clear vision of the relative (Ar, O_2 to vacuum and Ar to O_2) concentrations of ions in the laser-produced plasma can be obtained from a look at Figs. 6(a) and 6(b). From Fig. 6(a), we see that whereas in O_2 the amount of Li ions is always equal to or higher than in vacuum, the Li ions in Ar are, in general, below their concentration in vacuum and, consequently, below that in O_2 . Similar features are observed in Fig. 6(b) regarding Nb ions. In the latter case, the concentration of Nb ions far from the target reaches similar values in O_2 , Ar, and vacuum. The fact that, according to the model, there is more plasma ions in O_2 than in Ar might explain the lower crystallographic quality of the $LiNbO_3$ films grown within O_2 when compared to those grown in Ar.³

Finally, in Fig. 7 we have represented the relative concentrations of Li to Nb atoms and that of Li to Nb ions, respectively. We see that there are four times more Nb neutrals than Li neutrals. This proportion remains constant as we move away from the target independently of whether the

FIG. 7. Relative concentrations $N_{\text{Li}}/N_{\text{Nb}}$ in 1 Torr O_2 ($\blacktriangle$), 1 Torr Ar ($\bullet$), and vacuum ($\blacksquare$), and $N_{\text{Li}}^+/N_{\text{Nb}}^+$ in 1 Torr O_2 ($\triangle$), 1 Torr Ar ($\circ$), and vacuum ($\square$) as a function of the distance to target. The lines are a guide for the eye.

ablation process is performed within Ar, O_2 , or vacuum. However, the number of Li ions is slightly higher in Ar and O_2 than in vacuum.

The results discussed in this work are of a kinetic nature. This means that, starting from the known N_e and T_e values, we have considered the underlying radiative and inelastic collisional processes that lead us to estimate the concentrations of the different plasma species that can be subsequently activated by electronic collisions. We should, however, remember that, at sufficiently high pressures, hydrodynamic effects might additionally contribute to shape the lightest particle concentrations.^{18,19} The latter effect was clearly evidenced by Chaos *et al.*^{19,26} for the case of the delayed emitted ground Li atoms from LiNbO_3 . These Li atoms cannot be electronically activated since their time scale (of up to 1 ms after the laser pulse)¹⁹ is much longer than the one of the plasma electrons (1–2 μs).¹² Therefore, here we have not evaluated the concentration of the delayed emitted ground Li atoms.

IV. CONCLUSIONS

One of the most important results of this work is that ions rather than neutral atoms are the dominant species in the plasma produced after irradiating a LiNbO_3 target with a pulsed low fluence (1.2 J cm^{-2}) ArF excimer laser ($\lambda=193$ nm) in vacuum, O_2 , and Ar atmospheres. In general, the concentration of ions in O_2 is slightly higher than in Ar and vacuum, a result that might explain the lower crystallographic quality of the LiNbO_3 films grown within O_2 when compared to those grown in Ar. In addition, we found that whereas the amount of neutrals (Li and Nb) is the highest within O_2 , the concentrations of Nb neutrals in O_2 , Ar, and vacuum are about four times greater than that of Li.

We have also predicted the presence of excited Nb ions in the plasma. This prediction is qualitatively confirmed by previous experiments where some of the predicted excited Nb ions were detected by OES.

The relatively low average electron energies measured in these plasmas, together with the prediction of a fewer number of Li and Nb neutrals than ions and very high partial ionization degrees, suggest that an important part of the predicted ion concentration is not produced by electron–atom ionization events within the plasma. On the contrary, many plasma ions might have been produced in the LiNbO_3 crystal through a nonthermal ejection mechanism. However, the predictions stated in the present work indicating that, during irradiation of LiNbO_3 with pulsed low fluence UV lasers, the concentration of ions exceeds that of neutrals requires further experimental investigation and verification.

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- ¹Pulsed Laser Deposition, edited by D. B. Chrisey and G. K. Hubler (Wiley, New York, 1994).
- ²S. B. Ogale, R. Nawathey-Dikshit, S. J. Dikshit, and S. M. Kanetkar, J. Appl. Phys. **71**, 5718 (1992).
- ³J. A. Chaos, J. Gonzalo, C. N. Afonso, J. Perrière, and M. T. García-González, Appl. Phys. A: Mater. Sci. Process. **72**, 705 (2001).
- ⁴S. Amoroso, R. Bruzzese, N. Spinelli, and R. Velotta, J. Phys. B **32**, R131 (1999).
- ⁵T. N. Hansen, J. Schou, and T. G. Lunney, Europhys. Lett. **40**, 441 (1997).
- ⁶T. N. Hansen, H. Schou, and J. G. Lunney, Appl. Phys. Lett. **72**, 1829 (1998).
- ⁷T. N. Hansen, H. Schou, and J. G. Lunney, Appl. Surf. Sci. **138–139**, 184 (1999).
- ⁸B. Toftmann, J. Schou, T. N. Hansen, and J. G. Lunney, Phys. Rev. Lett. **84**, 3998 (2000).
- ⁹B. Thestrup, B. Toftmann, J. Schou, B. Doggett, and J. G. Lunney, Appl. Surf. Sci. **197–198**, 175 (2002).
- ¹⁰D. R. Ermer, S. C. Langford, and T. J. Dickinson, J. Appl. Phys. **81**, 1495 (1997).
- ¹¹S. Kano, S. C. Langford, and T. J. Dickinson, J. Appl. Phys. **89**, 2950 (2001).
- ¹²F. J. Gordillo-Vázquez, A. Perea, J. A. Chaos, J. Gonzalo, and C. N. Afonso, Appl. Phys. Lett. **78**, 7 (2001).
- ¹³F. J. Gordillo-Vázquez, A. Perea, and C. N. Afonso, Appl. Spectrosc. **56**, 381 (2002).
- ¹⁴F. J. Gordillo-Vázquez, J. Appl. Phys. **90**, 599 (2001).
- ¹⁵F. J. Gordillo-Vázquez and C. N. Afonso, J. Appl. Phys. **92**, 7651 (2002).
- ¹⁶J. T. Dickinson, S. C. Langford, J. J. Shin, and D. L. Doering, Phys. Rev. Lett. **73**, 2630 (1994).
- ¹⁷A. Perea, J. Gonzalo, C. N. Afonso, C. Vivien, and C. Leborgne, Appl. Phys. A: Mater. Sci. Process. **S69**, 141 (1999).
- ¹⁸D. J. Lichtenwalner, O. Auciello, R. Dat, and A. I. Kingon, J. Appl. Phys. **74**, 7497 (1993).
- ¹⁹J. A. Chaos, A. Perea, J. Gonzalo, R. W. Dreyfus, C. N. Afonso, and J. Perrière, Appl. Surf. Sci. **154–155**, 473 (2000).
- ²⁰A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules and Ions* (Springer, Berlin, 1980).
- ²¹<http://cfa-www.harvard.edu/amdata/ampdata/kurucz23/sekur.html>
- ²²W. Lochte-Holtgreven, *Plasma Diagnostics* (AIP, New York, 1995).
- ²³Y. B. Zeldovich and Y. P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (Academic, New York, 1966).
- ²⁴J. J. Shin, D. R. Ermer, S. C. Langford, and J. T. Dickinson, Appl. Phys. A: Mater. Sci. Process. **64**, 7 (1997).
- ²⁵C. N. Afonso, F. Vega, J. Gonzalo, and C. Zaldo, Appl. Surf. Sci. **69**, 149 (1993).
- ²⁶J. A. Chaos, R. W. Dreyfus, A. Perea, R. Serna, J. Gonzalo, and C. N. Afonso, Appl. Phys. Lett. **76**, 649 (2000).