Effect of Ar and O₂ Atmospheres on the Fundamental Properties of the Plasma Produced by Laser Ablation of Lithium Niobate

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The influence of gas atmospheres (at 1 torr) of different natures, both reactive (O₂) and inert (Ar), on the spatial evolution of the electron temperature (T_e) and electron density (N_e) of the plasma generated by laser ablation of a LiNbO₃ target is evaluated by optical emission spectroscopy techniques. It is found that the behavior of N_e in the plasma produced in vacuum, argon, and oxygen atmospheres exhibit quite different trends as a function of the distance from the target to the substrate, but the behavior of T_e is nearly constant. The spatial constancy of T_e in all the atmospheres studied is probably related not only to the low laser irradiance used (0.06 GW cm⁻²), but also to a possible collisional decoupling of the heavy species in the central part of the expanding plasma plume where a low pressure region is formed. The fact that N_e is lower in Ar than in O₂ indicates the presence of fewer positive ions in the plasma generated in Ar. The impact of this result on the better crystallinity observed in the LiNbO₃ films grown in Ar is also discussed.

Index Headings: Pulsed laser ablation; Lithium niobate; Argon and oxygen atmospheres; Plasma diagnosis.

INTRODUCTION

Pulsed laser deposition (PLD) has become a very promising tool for both advanced micromachining and thin film deposition. Among the parameters involved in the PLD processes, the laser fluence together with the background gas pressure (and nature) and the distance at which the substrate is located are relevant variables influencing the film growth process. Moreover, the ablation of solid targets produces, in most cases, a luminous plasma formed by neutral and ionized species whose expansion dynamics have been widely studied in order to understand the physical mechanisms controlling the thin film deposition process and properties.¹ Nevertheless, a very limited number of works have focused on the study of the fundamental plasma parameters, such as the electron temperature and electron density, or the nature of the dominant plasma excitation and ionization processes in different spatial and temporal regions.^{2–6} Although they are essential to evaluating the energy and material transport in the plasma, as well as to understanding the plasma reactivity in connection with its effectiveness in the processes of thin-film growth and composition, such studies have only been performed in ablation of metals,^{2,3} graphite,⁴ and YBa₂Cu₃O₇.⁵

Lithium niobate (LiNbO₃) is a well-known material with excellent nonlinear properties of interest for many applications that normally require the production of high quality thin films.⁷ Although PLD has proven to be one

of the most successful techniques in growing complex oxide materials,⁸ the films deposited by ablation of LiNbO₃ in vacuum or low pressure (<1 torr) atmospheres are often found to be Li deficient.^{9,10} However, recent results indicate that when the growth is carried out at a pressure of about 1 torr, independent of the nature of the ambient atmosphere used (either inert or reactive), the LiNbO₃ films grow stoichiometrically, though their crystallinity is slightly better when using Ar.¹¹

We reported earlier on a spectroscopic study of the light emitted from the plasma formed by laser ablation of a LiNbO₃ single crystal in vacuum. These investigations led to the determination of the variation of both N_e and T_e as a function of the distance to the LiNbO₃ target and the time after the laser pulse.⁶ Surprisingly, we found that T_e did not change with space and time, that is, as opposed to the behavior of T_e measured from laser ablation in vacuum of metals,^{2,3} graphite,⁴ and YBa₂Cu₃O₇.⁵ The space–time constancy of T_e was explained in terms of the atom–atom collisionless plasma expansion. However, it is interesting to investigate whether any of these constancies of T_e persist when a gas environment is used during laser ablation of LiNbO₃ and other types of materials. This research would be of interest because there are a rather limited number of works, or simply none, like in the case of the laser-produced plasma during ablation of LiNbO₃, on the effect of a gas's pressure and its nature (either reactive or inert) on the evolution of the N_e and T_e of the laser-produced plasma in PLD processes.

The aim of this work is to investigate the influence of a gas environment on the properties of the plasma formed by ablation of LiNbO₃ and to connect this influence to the properties of the synthesized films. We report the effects of using Ar and O₂ atmospheres at 1 torr on the spatial evolution of N_e and T_e . These effects will be compared to the properties of the plasma produced in vacuum. The T_e is determined by quantifying the relative emission line intensities of successive ionization stages of Nb atoms while Stark-broadened profiles of neutral Li atoms are used for quantifying N_e .^{12–14} The influence of the fundamental properties of the plasma on the quality of the synthesized LiNbO₃ films is finally discussed.

EXPERIMENTAL

The plasma was generated by ablation of a LiNbO₃ single crystal using an ArF excimer laser beam ($\lambda = 193$ nm) with a full width at half-maximum (FWHM) pulse duration ≈ 20 ns and a repetition rate of 10 Hz. The target was mounted in a rotating holder and placed in a chamber evacuated to a residual pressure of 6.0×10^{-7} mbar.

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Afterwards, a gas environment (either Ar or O₂) was introduced into the chamber until the pressure was equilibrated to 1 torr. The angle of incidence of the laser beam was 45°, and the laser energy density at the target surface was fixed at 1.2 J cm⁻² (irradiance ~0.06 GW cm⁻²), this energy being the one typically used to grow stoichiometric LiNbO₃ films.¹¹ The plasma formed during the laser ablation process was ×2 imaged onto the 30-μm entrance slit of a 0.75-m monochromator. To align and calibrate the monochromator, a He-Ne laser beam and the light from a Li hollow cathode lamp were both set parallel to the target surface following the same path as the light emitted by the plasma. The former allowed us to align the spectrometer perpendicular to the beams, and the latter provided the spectrometer resolution by measuring the linewidth of the 670.8-nm Li(I) line, which was 0.05 nm. The plasma image was scanned along the normal to the target with a spatial resolution of 0.18 mm, as reported elsewhere.¹⁵ The light was finally collected by a photomultiplier (15-ns rise time) connected to a boxcar averager/gated integrator. The gate width of the boxcar was set wide enough (variable between 1 and 15 μs depending on the specific emission transient duration) in order to collect a time-integrated signal, as described elsewhere.⁶ All experimental data was the result of an average of 10 pulses in order to minimize the small fluctuations of the plasma intensity caused by the fluctuation of the pulse energy output of the laser, which was about 3%. The results presented here start at a distance of 2 mm from the target to be sure that the contribution from the continuum can be neglected.¹⁶ Moreover, taking the spectrometer resolution from Eq. 1 below, we see that N_e must be greater than approximately 1×10^{16} cm⁻³ (which is the value of the electron density that corresponds to the instrumental linewidth) before the Stark-broadened linewidth will exceed that of the instrument. This means that the measurements performed at low electron density ($<2.5 \times 10^{16}$ cm⁻³) should be taken qualitatively because they are distorted by the instrumental broadening of the spectrometer.

RESULTS

Estimation of N_e using Stark broadening of spectral line profiles of an isolated atom or singly charged ion is a well-established and reliable technique¹²⁻¹⁴ used in many contexts, including laser plasma studies.¹⁷⁻¹⁹ In general, both Doppler and Stark broadening can contribute to spectral line broadening. However, the effect due to Doppler broadening (~0.12 Å at FWHM) can be neglected when compared to the Stark broadening resulting from collisions with the charged particles that dominate for plasma densities above 10^{14} cm⁻³.¹⁴ Stark broadening of well-isolated lines from neutral atoms is predominantly caused by electron impact, the FWHM of the Stark-broadened lines, $\Delta\lambda_{1/2}$, being related to N_e (in cm⁻³) by:¹⁴

$$\Delta\lambda_{1/2} = 2W \left[\frac{N_e}{10^{16}} \right] \text{Å} \quad (1)$$

where W is an electron impact parameter that is a weak function of the temperature and changes by a factor of less than 2 over the temperature range 10 000–80 000 K. In the case of the Li(I) transition considered in this work,

FIG. 1. Time-integrated N_e as a function of the distance to the target in vacuum (■), and in Ar (▲) and O₂ (●) atmospheres at a pressure of 1 torr. The dashed line shows a $1/d$ fit of the experimental data under vacuum conditions and the solid lines are a guide for the eye. The inset shows a typical Stark-broadened line of the Li(I) transition at 610.3 nm measured at 7 mm from the target. The FWHM of this line is used to determine the spatial evolution of the electron density.

for the 610.3-nm doublet ($3d^2D_{3/2,5/2} \rightarrow 2p^2P_{1/2,3/2}$), we have used $W = 0.216 \text{Å}$ (for $T_e = 10\,000$ K) to determine N_e .^{13,14} An alternative procedure to determine N_e would be to measure the Stark shift ($\Delta\lambda_{\text{shift}}$) associated with the 610.3 nm line of Li(I). In order to do this, we would have had to use an expression similar to Eq. 1 above, but substituting $2W$ for the coefficient D . However, the dependence of D on T_e is stronger than that of W and it can not be neglected. In addition, the available theoretical values of D are somewhat inferior (less accurate than W).¹⁴ Because of these reasons, the use of line shifts as a diagnostic method to determine N_e is not recommended¹⁴ (very accurate T_e measurements are needed to have the precise D dependence on T_e).

Figure 1 shows N_e calculated through Eq. 1 in vacuum, and in Ar and O₂ ambient atmospheres as a function of the distance to the target surface. The inset in Fig. 1 shows a typical broadened line of the Li(I) transition at 610.3 nm as recorded in our experiment. The N_e values in vacuum are found to decrease rapidly with distance.⁶ They are reasonably well fitted by a $1/d$ function (see Fig. 1), in agreement with the predictions of the plume expansion models proposed for free expansion (valid only under vacuum conditions).²⁰ This N_e space dependence is very similar to that reported earlier for plasmas produced in laser ablation of graphite⁴ and YBa₂Cu₃O₇⁵ for similar space intervals, though much higher power density levels were used in those works. The introduction of an ambient atmosphere in the processing chamber usually leads to enhancement of the plasma emission. This enhancement depends on the type of gas as well as on the gas pressure. We see in Fig. 1 that N_e in O₂ is always higher than that found both in vacuum and in an Ar atmosphere. It is also seen that it presents a maximum at around 5 mm from the target to reach values that are close to those obtained in vacuum and Ar for $d \approx 12.5$ mm. In contrast, the N_e found in Ar atmosphere is nearly constant in the range of distances studied.

The determination of T_e can be performed by measuring the ratio of two line intensities belonging to the same atomic or ionic species. However, two lines of the same

FIG. 2. Time-integrated T_e as a function of the distance to the target in vacuum (■), and in Ar (▲) and O₂ (●) atmospheres at a pressure of 1 torr. The solid lines are a guide for the eye.

species (with the same ionization stages) are nearer in energy than if they belong to different ionization stages, and thus line ratios within a given atom or ion normally do not provide very precise temperature measurements.¹³ Therefore, accurate determination of T_e is done by using the ratio of two line intensities from successive ionization stages of the same element. Assuming local thermodynamic equilibrium (LTE), the ratio of such line intensities is given by^{12,13}

$$\frac{I_1}{I_2} = \left(\frac{f_1 g_1 \lambda_2^3}{f_2 g_2 \lambda_1^3} \right) (4\pi^{3/2} a_0^3 N_e)^{-1} \left(\frac{kT_e}{E_H} \right)^{3/2} \times \exp \left(\frac{-E_1 + E_2 - E_\infty + \Delta E_\infty}{kT_e} \right) \quad (2)$$

where I_1 represents the line of the atom with the higher ionization degree, f_1 and f_2 are the absorption oscillator strengths, g_1 and g_2 are the statistical weights (or degeneracies of the states), a_0 is the Bohr radius, E_H is the ionization energy of the hydrogen atom, E_1 and E_2 are the excitation energies, and ΔE_∞ is the correction to the ionization energy E_∞ of the lower ionization stage due to plasma interactions. For high density plasmas (such as those encountered here), the correction factor in the ionization energy is given by

$$\Delta E_\infty (\text{eV}) = 3zb \frac{e^2}{4\pi\epsilon_0} \left[\frac{4\pi 10^6 N_e}{3} \right]^{1/3} \quad (3)$$

where $z = 2$ for the lowest ionization state, e is the electron charge (in C), ϵ_0 (in F m⁻¹) is the permittivity of the free space, N_e is in cm⁻³, and $b = 6.2414 \times 10^{18}$ is the energy conversion factor from Joules to eV. In order to determine T_e , the Nb(II) 478.9-nm and Nb(I) 407.97-nm lines were measured following the same procedure as in the case of the Li(I) line. The spectroscopic constants for the two Nb lines were taken from Ref. 21, and we have assumed a partially optically thin plasma as a first approximation, that is, the plasma is optically thin only for some spectral lines.

Figure 2 shows the dependence of T_e on the distance to the target surface in vacuum, Ar, and O₂ atmospheres (both at 1 torr). We found that, as opposed to what has

been reported for plasmas produced by laser ablation of metals,^{2,3} graphite,⁴ and YBa₂Cu₃O₇,⁵ T_e is almost constant (within experimental error) when increasing the distance to the target. This result is even more interesting because it looks independent of whether it is in vacuum or in a gas environment (either reactive (O₂) or inert (Ar)). The T_e values in vacuum are systematically above the ones obtained in gas, although always within the error band.

In order to derive T_e , we have assumed the validity of LTE. This assumption is likely to be valid provided that electron-heavy particle (atom, ion, or molecule) collisions are very fast and dominate the radiative processes. This means that the collisional rates controlling the excitation/ionization and deexcitation/recombination of the particles in the plasma must exceed the corresponding radiative rates. However, if the escape of radiation was sufficiently high, it could seriously affect the collisional equilibrium implicit in the LTE assumption. A necessary (though not sufficient) condition for having LTE is that N_e (cm⁻³) $\geq 1.4 \times 10^{14} \times T_e^{1/2} \times (\Delta E)^3$.¹⁴ In our case, for the transition at 407.97 nm of Nb(I) with $\Delta E = 3.03$ eV and $T_e = 0.74$ eV, we determined that LTE might start to hold both in O₂ and Ar for $N_e \geq 3.35 \times 10^{15}$ cm⁻³, as happens in our case (see Fig. 1). Moreover, in a transient plasma like ours, LTE is assumed to exist if the time between collisions of the species is small (here, for instance, the time between electron-ion collisions is $\tau_{ei} \sim 2$ ps) compared with the time scale of any significant change in the plasma.²²

DISCUSSION

The study of the interactions in a laser-generated plasma expanding into an atmosphere is a much more complex gas dynamic and kinetic problem than that of the plasma expansion into vacuum. The expansion of a plasma into a gas environment generally involves the formation of shock waves²³ that interact with the gas ahead, influencing, in a still not well understood way, the properties of the films that are being grown. The N_e measured for the plasma expanding into vacuum and into an ambient gas exhibit quite distinct trends, indicating the different ionization and recombination mechanisms competing during the expansion processes into vacuum, Ar, and O₂ atmospheres. Assuming that the energy distribution of the free electrons in the plasma follow a Maxwellian distribution function, we can estimate the electron-atom ionization rate coefficients for the different species (Li, Nb, O, O₂, and, if an argon environment is used, Ar) most probably present in the expanding plasma plume. Such calculations have been performed for Li by taking into account the generalized expression proposed by Drawin²⁴ for analytic evaluation of electron impact ionization rate coefficients,

$$S_{ic} = 1.46 \times 10^{-10} \zeta_1 \left(\frac{I_H}{I_1} \right)^2 T_e^{1/2} (K) u_1 \Psi_1(u_1, \chi_1) \text{ cm}^3 \text{ s}^{-1} \quad (4)$$

where $\zeta_1 = 1$ denotes the number of equivalent electrons in the ground state, $I_1 = 5.4$ eV and $I_H = 13.56$ eV are, respectively, the ionization energy of the ground level of atomic lithium and of the hydrogen atom, $u_1 = I_1/kT_e$,

FIG. 3. Ionization rate coefficient of Li atoms as a function of the distance to the target for two gas environments, Ar (▲) and O₂ (●) at 1 torr. The solid lines are a guide for the eye.

and $\chi_i = 1 + (Z_{\text{eff}} - 1)/(Z_{\text{eff}} + 2)$ so that $\chi_i = 1$ ($Z_{\text{eff}} = 1$), where Z and $Z_{\text{eff}} = Z - N + 1$ are the atomic number and the effective atomic number (with N being the number of bound electrons in lithium). The function Ψ_1 also admits an approximate analytic expression,²⁴

$$\Psi_1(u_1, \chi_i = 1) \cong \left[\frac{e^{-u_1}}{1 + u_1} \right] \times \left[\frac{1}{20 + u_1} + \ln \left(1.25 \left\{ 1 + \frac{1}{u_1} \right\} \right) \right] \quad (5)$$

Taking into account the principle of detailed balance (a consequence of assuming LTE), we can derive the three-body electron-ion recombination rate coefficient as²⁵

$$\beta_{c1} = 3.32 \times 10^{-22} \left(\frac{1}{kT_e} \right)^{3/2} \exp \left(\frac{I_1}{kT_e} \right) \times S_{1c} \text{ cm}^6 \text{ s}^{-1} \quad (6)$$

We have assumed that the plasma is partially optically thin and this assumption has allowed us to derive Eq. 6 because the collisional processes prevail over the escape of radiation so that LTE remains valid. However, it is important to point out that if the escape of radiation from the plasma is high enough, a possible ionizational non-equilibrium can exist in the plasma, that is, the degree of ionization of the plasma might be out of its equilibrium value (S_{1c}/β_{c1}). Such deviation will depend on the balance between nonelastic electron-atom/molecule and electron-ion collisions and radiative processes. Therefore, the use of the principle of detailed balance would lead to some inaccuracies in the evaluation of the *real* rate of the three-body electron-ion recombinations.

Figures 3 and 4 show respectively the spatial evolution of the ionization and three-body recombination rate coefficients of Li and Li⁺ in a reactive (O₂) and in an inert (Ar) atmosphere at 1 torr. The fact that up to $d = 11$ mm, $S_{1c}(\text{O}_2) > S_{1c}(\text{Ar})$ together with $\beta_{c1}(\text{Ar}) > \beta_{c1}(\text{O}_2)$ is consistent with $N_e(\text{O}_2)$ being higher than $N_e(\text{Ar})$.

Earlier experimental results indicate that the emission intensity from lines with low excitation energy increases significantly for gas pressures above 5×10^{-2} mbar and distances from the target greater than 2 mm.²⁶ This increase of emission should be associated with species that have been excited during plasma expansion into the gas

FIG. 4. Three-body recombination rate coefficient of Li⁺ as a function of the distance to the target for two gas environments, Ar (▲) and O₂ (●) at 1 torr. The solid lines are a guide for the eye.

atmosphere by two principal mechanisms: atom-atom collisional excitation/ionization and electron-impact excitation/ionization and recombination.²⁷⁻³⁰ However, since the cross section of the former is about two orders of magnitude smaller than that of the latter,^{29,30} electron-impact processes control the excitation of the species as the plume expands, the electrons being produced by ionization of the ejected and external species. Since the ionization energy thresholds of O₂ and O are, respectively, 12.5 eV and 13.6 eV, both lower than the ionization energy threshold of Ar (~15.7 eV),³¹ a higher N_e is expected in O₂ than in Ar (see Fig. 1), and consequently, a higher emission intensity should also be expected in an O₂ environment. However, the available experimental results regarding emission of Li(I) (670.9 nm) and Nb(I) (408.0 nm) show instead a greater emission intensity in the case of an Ar atmosphere.²⁶ Therefore, there has to be another process that promotes the excitation of the ejected species in Ar gas. It is known that the presence of a foreign gas produces a plasma confinement^{27,29} and consequently, an increase in the density of the ejected species in the plume; the higher the mass of the foreign gas the stronger the confinement and therefore, the higher the density of the ejected species and the higher the probability of excitation. Because Ar is heavier than O₂, the confinement should be stronger in Ar, thus leading to a more intense optical emission, as recorded experimentally.

Another remarkable feature shown in Fig. 1 is the fact that $N_e(\text{O}_2)$ is greater than $N_e(\text{Ar})$ and therefore, since macroscopic electric neutrality is assumed in the plasma, the total number of positive ions in the plasma formed in an Ar environment is less than the one generated in O₂. It is well known that ion bombardment during film growth promotes the densification of the films but can also induce damage and thus deteriorate the epitaxial growth.³² The fewer number of positive ions found here when using an Ar atmosphere is thus consistent with the better crystallinity of the LiNbO₃ films grown in Ar than that of the films grown under the same conditions but in O₂.

The most striking result when comparing the present study to those reported earlier relates to T_e , as it remains nearly constant with the distance within the studied intervals (see Fig. 2). This weak space dependence of T_e

has been reported for long distances in experiments performed in vacuum and has been related to the fact that the cooling due to the expansion becomes in part compensated for by the energy released by the recombinations.^{4,5} However, in plasma expansions into gas, the T_e constancy might most likely have to do with two possible reasons: (1) the irradiance levels needed to ablate LiNbO₃ targets are so weak (0.06 GW cm⁻²) that the low energy gained by the electrons hardly allows further dissipation (this reason could also be valid for the vacuum case); and/or (2) since the species in the plasma have slightly different velocities, which makes them separate from each other as the distance increases, the electron-atom, and especially the atom-atom collision, probability decreases so that collision-induced cooling does not occur and thus the temperature remains almost constant.

Regarding reason (1), the electrons become thermalized very fast and they have such low mean energies that they are hardly pressure-dependent at such low power densities as opposed to what is a typical behavior in partially ionized gases with higher electron mean energies. Concerning reason (2), since LTE is assumed, the temperature of ions and neutrals should be similar to that of the electrons. This is consistent with the assumed atom-atom collisionless plasma expansion into vacuum for distances longer than 2 mm. When a plasma expands into an ambient gas, elastic and nonelastic atom-atom collisions are expected (especially at the leading edge of the plasma). However, atom-atom collisions are much less probable in the central part of the expanding plasma plume because, according to a recently proposed hypothesis,¹¹ at high enough pressures (of about 1 torr) the shock wave front pushes ahead the gas environment creating an inner region of the expanding plasma that is at lower pressure than the surrounding gas, thus providing the conditions for fewer atom-atom collisions.

In spite of the above reasons explaining the space constancy of T_e , there is not definitive experimental evidence to clearly conclude from the results presented here whether only one or both of them are correct and/or complementary. Therefore, whether the observed space T_e constancy is a general conclusion for plasmas generated by ablation of insulators in which defects play an essential role in the ablation process or whether it is related to the special kinetics of the LiNbO₃ plasma is not yet clear and needs further investigation, which is now underway.

CONCLUSION

The different space dependence of N_e in vacuum, Ar, and O₂ atmospheres is associated with the distinct ionization potentials of the considered gases and to the spatial evolution of the corresponding electron-atom ionization and electron-ion three-body recombination rate coefficients. The fact that $N_e(\text{O}_2)$ is higher than $N_e(\text{Ar})$ reveals the existence of more positive ions in the plasma generated in an O₂ environment than in that formed in an inert (Ar) gas, and this result is consistent with the better crystallinity of the films grown in Ar than those grown in O₂ reported earlier. In addition, it was found that in comparison with N_e , T_e shows in all cases (either vacuum or different gas atmospheres) a very similar trend, that is,

small values and very little dependence on the distance. Both features are most likely related to the atom-atom collisionless expansion of the laser-generated plasma from LiNbO₃ ablation and/or to the low laser power density used (0.06 GW cm⁻²) to ablate LiNbO₃.

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1. *Pulsed Laser Deposition*, D. B. Chrisey and G. K. Hubler, Eds. (John Wiley and Sons, New York, 1994).
2. J. M. Hendron, C. M. O. Mahony, T. Morrow, and W. G. Graham, *J. Appl. Phys.* **81**, 2131 (1997).
3. B. Toftmann, J. Schou, T. N. Hansen, and J. G. Lunney, *Phys. Rev. Lett.* **84**, 3998 (2000).
4. S. S. Harilal, C. V. Bindhu, R. C. Isaac, V. P. N. Nampoori, and C. P. G. Vallabhan, *J. Appl. Phys.* **82**, 2140 (1997).
5. S. S. Harilal, C. V. Bindhu, V. P. N. Nampoori, and C. P. G. Vallabhan, *Appl. Spectrosc.* **52**, 449 (1998).
6. F. J. Gordillo-Vázquez, A. Perea, J. A. Chaos, J. Gonzalo, and C. N. Afonso, *Appl. Phys. Lett.* **78**, 7 (2001).
7. *Properties of Lithium Niobate*, EMIS Datareviews Series No. 5 (IEEE, London, 1989).
8. C. N. Afonso, in *Materials for Optoelectronics: New Developments*, F. Agulló-López, Ed. (World Scientific, Singapore, 1995), Chap. 1, and references therein.
9. S. B. Ogale, R. Nawathey-Dikshit, S. J. Dikshit, and S. M. Kanetkar, *J. Appl. Phys.* **71**, 5718 (1992).
10. Y. Shibata, Y. Kanno, K. Kaya, M. Knai, and T. Kawai, *Jpn. J. Appl. Phys., Part 1* **34**, L320 (1995).
11. J. A. Chaos, J. Gonzalo, C. N. Afonso, J. Perrière, and M. T. García-González, *Appl. Phys. A*, paper in press.
12. H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic, New York, 1974).
13. H. R. Griem, *Principles of Plasma Spectroscopy* (Cambridge University Press, Cambridge, U.K., 1997).
14. G. Bekefy, *Principles of Laser Plasmas* (John Wiley and Sons, New York, 1976).
15. C. N. Afonso, F. Vega, J. Gonzalo, and C. Zaldo, *Appl. Surf. Sci.* **69**, 149 (1993).
16. J. Gonzalo, F. Vega, and C. N. Afonso, *J. Appl. Phys.* **77**, 6588 (1995).
17. D. A. Cremers, *Appl. Spectrosc.* **41**, 572 (1987).
18. R. Barbini, F. Colao, R. Fantoni, A. Palucci, and F. Capitelli, *Appl. Phys. A* **69**, S175 (1999).
19. M. Milan and J. J. Laserna, *Spectrochim. Acta, Part B* **56**, 275 (2001).
20. R. K. Singh and J. Narayan, *Phys. Rev. B* **41**, 8843 (1990).
21. C. H. Corliss and W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, NBS Monograph Vol. 53 (NBS, Washington, DC, 1962).
22. Y. B. Zeldovich and Y. P. Raizer, *Physics of Shock Waves and High Temperature Hydrodynamic Phenomena* (Academic Press, New York, 1966).
23. D. B. Geohegan, *Thin Solid Films* **220**, 138 (1990).
24. H. W. Drawin, *Collision and Transport Cross Sections*, Report EUR-CEA-FC 383 (revised), 1967.
25. J. A. Kunc and W. H. Soon, *Phys. Rev. A* **40**, 5822 (1989).
26. J. A. Chaos, Ph.D. thesis, Universidad Autónoma de Madrid, Madrid, Spain (2001).
27. H. F. Sakeek, T. Morrow, W. G. Graham, and D. G. Walmsley, *J. Appl. Phys.* **75**, 1140 (1994).
28. H. S. Kwok, *Thin Solid Films* **218**, 277 (1992).
29. H. P. Gu, Q. H. Lou, N. H. Cheung, S. C. Chen, Z. Y. Wang, and P. K. Liu, *Appl. Phys. B* **58**, 143 (1994).
30. C. Timmer, S. K. Srivastava, T. E. Hall, and A. Fucaloro, *J. Appl. Phys.* **70**, 1888 (1991).
31. *Handbook of Chemistry and Physics*, (CRC, Boca Raton, FL, 1997), 78th ed.
32. *Handbook of Thin Film Technology*, I. L. Maissel and R. Glang, Eds. (McGraw-Hill, New York, 1983 Reissue).