

## ENHANCED OXIDE EMISSION IN ELECTRODE-AIDED LASER DEPOSITION OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ THIN FILMS

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*Abstract.* Emission spectroscopy was used to study the effect of a polarized electrode on the properties of pulsed laser deposition plasmas. The presence of the electrode can preferentially excite oxides in high-density regions of the plasma: the near target region in vacuum, and behind the shock front in a gas atmosphere.

*Key words:* laser deposition, optical emission spectroscopy, oxide, electrode, laser ablation plasma.

### 1. INTRODUCTION

Pulsed laser deposition (PLD) is a relatively simple and versatile method that has proven its capability to produce a large variety of thin films, such as high- $T_c$  superconducting thin films, ferroelectrics, magnetic films, transparent conducting oxides [1–5]. Several techniques for improving the properties of laser-deposited thin films through additional activation of species in the plasma or on the substrate have been explored [6, 7]. Such an enhancement of the process may be obtained through a supplementary discharge and/or a magnetic field applied in the plasma, plasma irradiation with a second laser, use of a separate ion or neutral flux, etc. The effect of the activation is to alter properties of ions, such as ion energy and ion-to-atom arrival rate on the substrate, or those of oxide species.

The introduction of a polarized electrode between the target and substrate is a simple and efficient method of improving thin film properties [8, 9]. The subject of the present paper is the spectral analysis of the effects of a polarized electrode on the properties of PLD plasma species; these results are correlated with some fast-framing photo results. The study of the relative modification of spectral characteristics of neutrals, ions and oxides was made in different conditions: at various distances from the target, in vacuum and in 190 mTorr oxygen (a typical deposition pressure for high quality laser-deposited superconducting YBCO thin films), and for several magnitudes of positive and negative voltage.

The results show a complicated interplay between irradiation parameters. The most interesting one observed is that, under certain conditions, the oxide emission is greatly enhanced (in comparison to elementary neutrals and ions) in the presence of an applied voltage; the effect is present in vacuum as well as in an oxygen atmosphere.

Some phenomenological explanations are attempted to describe these effects, which could prove important in practical deposition conditions, since the presence of oxides seems to be essential for producing high-quality films [10].

## 2. EXPERIMENT

The setup used for the present experiments is given in Fig. 1. The irradiations were performed using a KrF laser with a pulse duration of 20 ns (FWHM). The beam was focused on the target using an  $f = 360$  mm lens, giving a pulse energy density of  $0.6\text{--}0.75$  J/cm<sup>2</sup>. The target was a stoichiometric YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) pellet. No substrate was present in any of the experiments. Investigations were made for vacuum ( $10^{-5}$  Torr) and 190 mTorr oxygen.

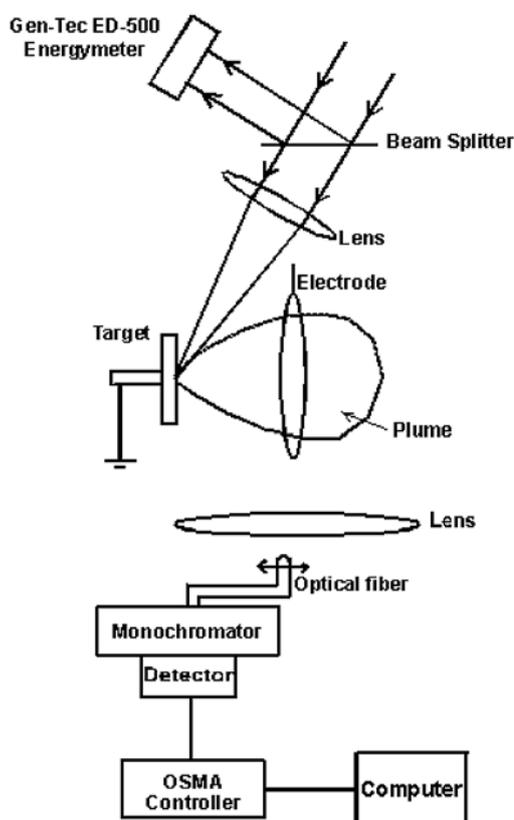


Fig. 1 – Schematic diagram of the experiment.

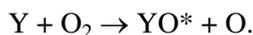
We used a copper ring electrode with a diameter of 2.5 cm placed 2 cm from the target. The electrode is parallel to the target and approximately centered on the laser spot on the target. Positive or negative voltages of 240 V or 450 V were applied to the electrode from a continuous source, the conducting target being connected to the source ground.

The spectra were obtained by imaging (with magnification 1) the plasma plume formed in front of the target, using an  $f = 300$  mm lens, onto an optical fiber connected to the entrance slit of a monochromator, which has its 50  $\mu\text{m}$  slit parallel to the target surface. Plasma emission was thus collected parallel to the target surface, giving spatially resolved results for different distances from the target: 0.5 cm, 1 cm and 1.5 cm. The emission was integrated over the total lifetime of the plume. The 320 mm grating monochromator (MC-25NP Ritsu Oyo Kogaku) has 1200 grooves/mm and a spectral range of 300–700 nm (compatible with that of the optical fiber). The detector, having 700 channels with about 0.055 nm/channel (this is an average value, because there is a slight variation with wavelength), is connected to a Princeton Instruments OSMA detector controller and a computer for spectrum acquisition. The system was calibrated using a Hg lamp.

### 3. RESULTS AND DISCUSSION

An examination of the spectra obtained in the presence of a biased electrode reveals an increase of spectral emission intensity compared to that in its absence. Greater plume brightness is also evident in fast-framing photographs, especially in vacuum, due both to the increase of intensity at a given moment, and to the increase of the total duration of emission.

Oxide emission is present in vacuum, for all the distances from the target which we investigated. This indicates that in the energy domain used in our experiment, oxides in an excited state are most probably emitted from the target. Similar results were obtained in the absence of an electrode [11]. Moreover, experiments made in the absence of an electrode in an oxygen and nitrogen atmosphere show that the difference between oxide emission for the two gases is not great (for all distances considered). In many articles it is suggested that excited oxides are mainly formed through the reaction [12]:



Our results, however, lead to the conclusion that the above gas-phase oxidation reaction is not the major source of excited oxides. It is considered that the reactivity of elementary species increases with laser energy density, but that it also depends on the type of expansion (and therefore on spot size, not on energy density alone [13]); in the conditions of a higher reactivity, the gas-phase generation

of oxides is favored. In our case, the energy density domain used may be too small to promote considerable gas-phase oxidation reactions.

We investigated the nature of the emissive species; the most representative lines and bands are given in Table 1. The lines observed in the spectrum are mostly atom and ion lines of Y and Ba, the most intense ones being due to BaII; a few neutral Cu lines are also present. No OI lines, OII lines or molecular oxygen bands appear. Several BaO and YO emission bands are present. Emission in the spectral domain of an  $O_2^+$  band has been noted, but it is superposed over YO emission bands. This does not allow us to certify the presence of excited  $O_2^+$  in the plasma.

*Table 1*

Principal spectral emission lines identified in our experiments. The intensities given are those observed 1.5 cm from the target, in vacuum, with + 450 V applied to the electrode. Wavelengths given for the oxides are band heads. Source used for line identification: CRC Handbook of Chemistry and Physics, 72nd Edition, editor D. R. Lide, (1991–1992)

Species	$\lambda$ [nm]	Intensity [arbitrary units]
YII	371.03	6763
YII	377.43	5300
BaII	389.18	3584
YI	407.74	3678
YI	412.83	8107
YII	439.80	4543
YI	452.73	2713
BaII	455.40	16 467
BaII	493.41	18 297
CuI	521.82	923
YI	546.65	1350
BaI	553.55	2295
BaII	585.37	5773
BaO	564.41	246
YO	597.20	520.4
YO	601.99	568
BaII	614.17	12 350
BaII	649.69	6587

The relative intensity of lines from different species depends on various parameters, as will be discussed below.

One of the parameters affecting the spectral characteristics is the magnitude of the applied voltage. For the laser energy density domain considered, the increase

of emission from 0 to  $\pm 240$  V is small (from 0 to + 240 V there is practically no change). The greatest effect is upon increase from 240 V to 450 V.

The dependence on voltage sign is complex, depending on distance from target and voltage magnitude. In vacuum, a voltage bias of  $-240$  V applied on the electrode always leads to spectra more intense than + 240V, but + 450 V leads to more intense emission than  $-450$  V in most cases.

The dependence of the spectra obtained in vacuum on the distance from the target has interesting characteristics. In the near-target region (0.5 cm), + 450 V leads to lines up to three times more intense than  $-450$  V (the greatest difference being for the most intense lines) (Fig. 2). There is, however, an important exception: oxide emission is more intense for  $-450$  V than for + 450 V . The difference is visible in the range 595–605 nm, but also for 610–620 nm (although in the latter case there is a strong BaII line superposed over the oxide bands). Oxide emission is

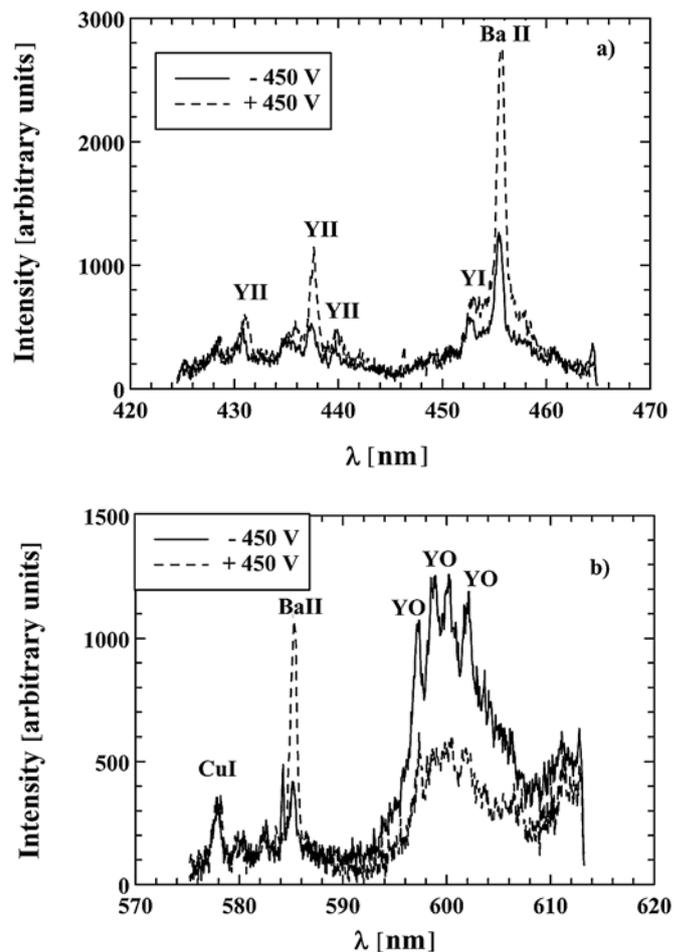


Fig. 2 – Spectra observed in the near-target region (0.5 cm from the target), in vacuum, for + 450 V and  $-450$  V, in two different wavelength domains.

also more intense than neutral atom and ion lines in the same spectral range (as a matter of fact, they are more intense than all but a few very strong BaII lines over the entire spectral range studied). This effect is only observed when the biased ring is placed in the plasma; the experiments we made in the absence of an electrode, in various conditions (some being similar to the ones described here) always result in relatively low-intensity oxide emission.

From 0.5 to 1 cm there is a decrease in emission intensity, which is characteristic for plasma expansion in vacuum in the absence of an electrode, as well. The decrease is similar for elementary species for both polarizations (up to two times); however, the decrease of oxide emission for  $-450$  V is greater (three to four times).

Close to the electrode region (1.5 cm from the target) the emission increases again (compared to 1 cm), for positive as well as negative voltages; this is obvious in fast-framing photos, as well. This contrasts with the no-electrode case, when there is a continuous decrease of emission beyond the target. For both 1 cm and 1.5 cm,  $+450$  V leads to more intense lines than  $-450$  V (including for oxide emission). In these regions, where the plasma density decreases markedly in vacuum through expansion, the phenomenon of intense oxide emission observed in the near-target region is no longer present.

In conclusion, in vacuum there is an intense oxide emission characteristic for the high density near-target region, in the case of a negative voltage applied to the electrode. A simple explanation could be proposed. The increase of emission intensity in the presence of an electrode is presumed to appear due to greater species excitation produced by electron collisions with plasma constituents [14, 15]. In the case of negative voltages, electrons are strongly accelerated to the dense near-target region, and excite existing oxides. This process of excitation followed by radiative deexcitation is for some reason more favorable for oxides than for elementary species in these conditions. In the laser energy density domain used, oxides are emitted from the target; many oxides are not emitted in an excited state, and are only excited by electron collisions. Emission spectroscopy alone cannot completely clarify these processes, a complementary analysis of non-emitting species being necessary. In the electrode region, the intense emission is due to other species, and not to oxides.

In the presence of a gas atmosphere, some aspects differ from the vacuum case. The experiments, carried out in 190 mTorr oxygen, were only made for positive and negative voltages of 240 V, and not greater, in order to avoid a continuous discharge between laser pulses.

Whether or not an electrode is present, in an oxygen atmosphere at this pressure hydrodynamic effects produce a highly luminous front (suggestive of a shock front) at the leading edge of the plasma [11]; the front is a result of slowing of emitted target species through collisions with background gas molecules, and accumulation of these species into a dense region behind the shock front formed in

the gas. In our experimental conditions, this front accounts for most of the emission observed at 1 and 1.5 cm from the target.

Both for distances of 1 cm and 1.5 cm from the target,  $-240\text{ V}$  leads to more intense emission than  $+240\text{ V}$  for all spectral characteristics (as in the vacuum case presented before). Some results for 1 cm are presented in Fig. 3; spectra obtained 1.5 cm from the target are similar. Oxide lines are more intense than neighboring neutral atom and ion lines (and most other lines of the spectrum, except some BaII lines) for both distances. It is interesting to note that strong oxide emission appears in the high-density regions of the plasma: the near-target region in vacuum, and the region behind the shock front in a gas atmosphere. The difference between results in an oxygen atmosphere and in vacuum is that in the latter case intense oxide emission is for both negative and positive electrode voltage, whereas in the former only for negative.

Fast-framing photography indicates that a visible effect of the electrode on the plasma is from the moment the expanding plasma species reach the ring; a discharge

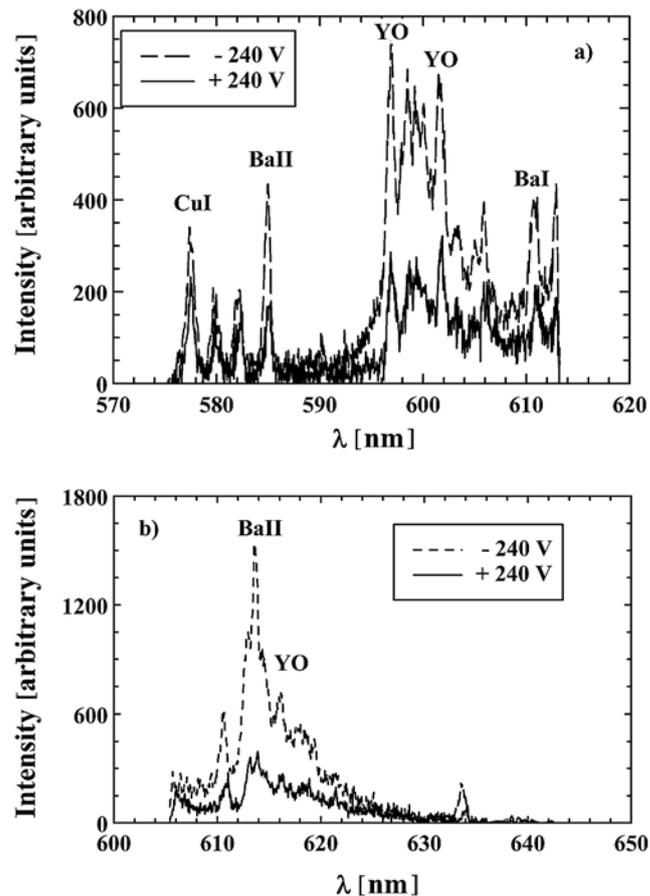


Fig. 3 – Spectra observed 1 cm from the target in an oxygen atmosphere of 190 mTorr, for  $+240\text{ V}$  and  $-240\text{ V}$ , in two different wavelength domains.

through the plasma is initiated at this moment. This suggests that the decisive role in the processes generated by the presence of the electrode is that of the current, rather than that of the electric field. The hypothesis is also supported by the fact that introducing a large enough resistor in the electrode circuit eliminates any visible effect of the ring on plasma expansion. Due to the fact that the direction of plasma expansion gives the problem a non-symmetrical character, the discharge current, and therefore the phenomena in the plasma, will depend on electrode polarity.

There are more possible interpretations for plasma behavior in the presence of an oxygen atmosphere. The first is that in the absence of an electrode, some oxides are formed by gas-phase chemical reactions between Y and O<sub>2</sub>, but most of them do not emit radiation (either because they are not formed in an excited state, or because they do not de-excite radiatively). Pramanick and Narayan [9] do in fact state that for molecular species nonradiative relaxation dominates for collisions with gas molecules, while for neutral or ionic atom beams such collisions lead to radiative relaxation. In the presence of an electrode, the spectral emission of these oxides could be preferentially enhanced through electron collisions; the “true” effect of chemical oxide-forming reactions can thus be seen.

The second interpretation is that the presence of a polarized electrode somehow enhances formation of oxides through chemical reactions between ablation products and ambient gas at the contact front. The effect depends on voltage polarity because it is a function of the relationship between the expansion direction of ions and electrons and the direction of the applied electric field [15]. If this second hypothesis is valid, then the increase of YO emission should be associated with a decrease of atomic and ion line emission of Y and O or O<sub>2</sub>. We did observe some relative decrease of YII lines (490.01 nm, 520.29 nm), but could not associate this with the variation of OI and OII lines, which are absent in our spectrum. The relative decrease of YI and YII can at any rate expected to be small, given the wealth of these lines compared to YO emission, so that it is not possible to verify this hypothesis using visible emission spectroscopy alone.

Molecular oxygen ion formation has been suggested as a possible explanation of improved thin film properties in the presence of an electrode [16]. Our spectra reveal some emission that could be attributed to O<sub>2</sub><sup>+</sup> at 597.3 nm [17], which only appears in an oxygen atmosphere in the presence of an electrode, but it is superposed over YO emission bands (see Figs. 2b and 3a).

#### 4. CONCLUSIONS

Complex phenomena were noticed when an electrode with an applied dc voltage is introduced in the laser ablation plasma. The most interesting is that the

presence of the electrode can preferentially excite oxides under certain conditions. This enhanced oxide emission is characteristic for the high-density regions of the plasma: the near-target region in vacuum, and the region behind the shock front in a gas atmosphere. This result is potentially important for improving the quality of laser-deposited high- $T_c$  thin films. The electrical properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  depend strongly on the oxygen content. Therefore, the amount of oxides which exists in the target-substrate region, as well as their reactivity, are very important.

Most phenomena may be described considering the additional excitation produced by electron collisions in the electrode-target region, after a discharge is initiated in the plasma. The behaviour of emissive species alone, however, cannot fully explain why the formation of excited oxides is favored over that of elementary species, or why a positive electrode bias leads to stronger emission than a negative one for 450 V, and weaker emission for 240 V. The clarification of these points, and a more comprehensive description of the process, warrants the use of complementary methods of plasma analysis.

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