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Laser ablation of ceramic oxides in the presence of a RF pulsed oxygen plasma

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Abstract

We have carried out laser ablation of ceramic targets with synchronous pulsed injection of molecular oxygen gas ionized and dissociated by a radio-frequency discharge. Time- and space-resolved optical absorption spectroscopy diagnostics reveals that the conditions occurring in conventional ceramic laser deposition experiments, i.e. with a continuous flow of molecular oxygen, can be recovered in the novel configuration. This approach allows us to reduce sample exposure to oxygen, which may be useful to prevent substrate oxidization in coated conductor fabrication.

Keywords: Pulsed laser deposition; Coated conductors; High temperature superconductors; Absorption spectroscopy

1. Introduction

One of the most appealing peculiarities of pulsed laser deposition (PLD) is the occurrence of collisional effects during the expansion of the ablated plume. In particular, when PLD takes place in a gaseous environment, such effects lead to modify the plume stoichiometry, thus affecting the composition of the deposited material. This circumstance is fully exploited in the so-called reactive-PLD [1]. However, the possibility to enhance the oxygen stoichiometry in high temperature superconductive (HTS) films by a low pressure molecular oxygen environment has been recognized since from the early works [2] as one of the key points to attain good quality oxide films.

As a matter of fact, the environment turns out to be responsible for a variety of processes. First of all, dynamics of the expanding material is strongly modified [3], elemental fragmentation of the ablated material is promoted with direct consequences on film morphology [4], and a blast wave is formed leading to remarkable species excitation [5]. On the other hand, all such processes can directly drive modifications of the plume composition, as widely observed in the past, for instance by optical emission [6] and ion-mass spectroscopy [7].

More recently, by using time- and space-resolved absorption spectroscopy for atomic [8] and molecular [9] oxygen during PLD of ceramic and metal targets, we have found different reactive collisional channels [10] leading to an efficient dissociation of O_2. Due to the strong reactivity of elemental oxygen, our findings may explain formation of molecular oxides and oxidized clusters, whose arrival onto the substrate can enhance oxygen stoichiometry in the film.

However, some situations exist where an excess of oxygen can lead to detrimental effects. The case of HTS deposition onto metal substrates (the so-called coated conductors) can be considered as a relevant example. Oxygen must be injected into the deposition chamber in order to get the correct structure in the HTS layer (typically, a YBCO thin film). On the other hand, the metal substrate can easily undergo surface oxidization that prevents the attainment of a smooth and homogeneous morphology, leading to poor functional properties.

The search for optimal deposition conditions in similar situations gave us motivations to explore the feasibility of PLD with synchronous injection of atomic oxygen, produced through radio-frequency (RF) dissociation of an O_2 pulse. In situ diagnostics of the process through absorption spectroscopy is presented here in order to demonstrate that the usual conditions of conventional PLD for ceramic materials (i.e. with a continuous flow of molecular oxygen) can be roughly

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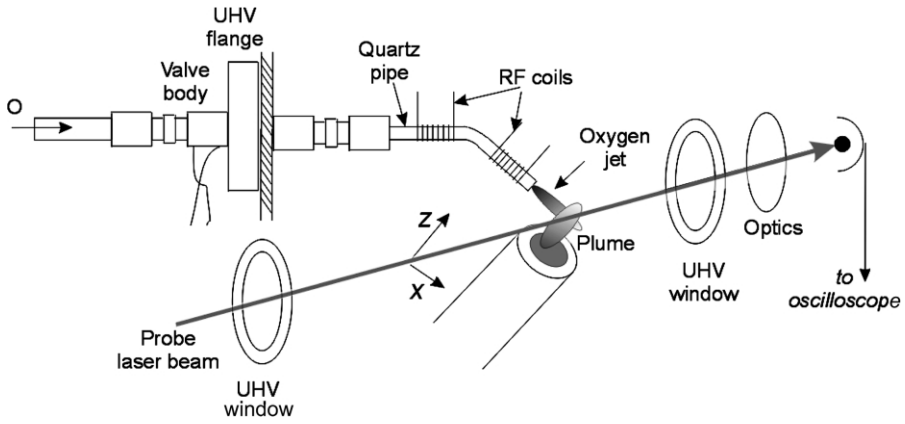

Fig. 1. Sketch of the experimental apparatus for pulsed injection in the presence of RF excitation and for in situ diagnostics by optical absorption.

reproduced, accompanied with a remarkable decrease of the sample exposure to oxidizing agents.

2. Coated conductor fabrication by PLD

Our coated conductor prototypes consist of a YBCO/YSZ bilayer deposited by PLD onto a NiFe (50:50) flexible substrate, cold rolled to achieve biaxial texturing. Sample characterization revealed encouraging structural properties [11], but the electrical performances, in terms of transition width and critical current, turn out far from the excellent figures expected for YBCO. We ascribed such a discrepancy between structural and functional features mainly to oxidization of the metal substrate that occurs during the deposition of the YBCO layer in the presence of O_2. Indeed, even if the YSZ layer should act as a barrier against oxygen diffusion, the high temperature experienced by the substrate during the deposition and its high reactivity, along with the presence of defects in the YSZ film, can lead to a remarkable growth of Fe-oxides.

An oxygen excess (i.e. use of O_2 pressures above 0.4–0.5 mbar) produces macroscopic effects, with diffused cracks and holes in the YBCO layer. However, even by keeping the oxygen pressure at the minimum values compatible with superconducting YBCO formation (0.1–0.3 mbar), an inhomogeneous film composition is detected at the level of the single grain [12]. Thus, a strategy to reduce exposure to oxygen of the sample during its growth is expected to improve significantly the quality of the coated conductors, also in view of possible applications.

Pulsed injection of O_2 into the plume expansion region has been already proposed in the past [13], but the average O_2 pressure in the chamber during the plume expansion may turn out too small to induce significant molecular dissociation processes leading to formation of the highly reactive atomic oxygen (either neutral or ionized). In order to improve the density of atomic oxygen, we have exploited a RF discharge, as recently carried out in, for instance, nitride film deposition [14]. RF driven collisional and plasma processes are known to efficiently lead to O_2 dissociation, especially in the presence of an inert buffer gas [15].

3. Experimental

We use a standard apparatus for PLD, based on a XeCl excimer laser (pulse duration $\sim$17 ns) and a stainless steel deposition chamber evacuated by a rotary and a diffusion pump (with base pressures $<10^{-2}$ and $<10^{-7}$ mbar, respectively). Pulsed gas injection is provided by a solenoid valve (General Valve Series 1, with a 0.5-mm nozzle), fed by O_2 gas at low pressure ($\sim$2 bar). Full synchronization of the valve operation with the laser shot is provided by specific electronic circuitry, which allows us to set independently the duration and delay of the valve opening. Due to the relatively slow mechanical rise-time of the solenoid (hundreds of microseconds), the electronic pulse controlling the opening must be sent in advance with respect to the ablating laser shot. For this reason, the delay will be indicated in the following with negative figures.

The output of the valve is connected to a quartz tube (OD 6 mm, ID 2.5 mm, length 180 mm) pointing at the plume, as sketched in Fig. 1. We note that our configuration is similar to the so-called crossed-beam laser ablation [1,16]. In any case, we stress that the dynamics of our pulsed gas beam is not expected to exhibit a supersonic character because of geometrical and size reasons. The residual pressure of oxygen in the substrate region during the pulsed valve operation cannot be easily ascertained. However, estimations based on time-averaged measurements by vacuum gauge suggest that, depending on the pulse duration (typically, hundreds of microseconds), the repetition rate (typically, below 10 Hz) and the pumping conditions, values more

than one order of magnitude smaller than in conventional PLD can be achieved.

A RF plasma is produced by two copper wire coils (17 rounds) wounded around the quartz tube. The coils are connected to a home made cw RF oscillator in a push–pull configuration (frequency ~23 MHz, power ~1 W). In order to reduce problems associated with impedance matching between the oscillator and the coils (the oscillator being outside the vacuum chamber, and the electrical connection being made by a vacuum feedthrough), a thermionic tube is exploited in the final stage of the oscillator. Furthermore, a controlled cw flow of a buffer gas can be injected into the chamber through a needle valve.

The set-up for the in situ diagnostics of the process has been already presented elsewhere [8,10]. Briefly, a diode laser provides radiation approximately 777 nm, resonant with the transition $3s^5S_2 \rightarrow 3p^5P_3$ of atomic oxygen. The weak probe radiation is sent, through an optical fiber, across the plume and the transmitted intensity is collected, after crossing some optical components mainly used to reduce the optical emission from the plume, by a photodiode (Fig. 1). The photodiode signal is recorded by a digital oscilloscope triggered by the arrival of the ablating laser shot onto the target. Signals are typically averaged over hundreds of ablating shots to improve the signal-to-noise ratio, and by acquiring a sequence of data with the probe beam on and off, the temporal behavior of the local oxygen absorption Abs(t) (normalized, i.e. Abs = 0 and Abs = 1 for null or full absorption, respectively) can be derived [8]. The probe beam (1-mm diameter) can be scanned within the plume range, and by repeating measurements at different positions information on the local oxygen absorption, dependent on the local oxygen density, can be obtained.

4. Results and discussion

We have already demonstrated that, in the usual conditions of PLD, i.e. with a continuous flow of O_2 into the deposition chamber, efficient processes occur leading to a local increase of atomic oxygen stemming from environment gas dissociation. Those processes have been ascribed [10] to both prompt electron production and, mostly, to the partial development of a blast wave following plume expansion. In addition, when a ceramic target is ablated, we have to take into account direct release of oxygen from the target, which also contributes to the observed absorption signals.

An example of our results is presented in Fig. 2, where Abs(t) is shown as measured at a distance $z = 6$ mm from the target (along the plume axis, i.e. for $x = 0$, Fig. 1) during PLD with pulsed injection (pulse delay-2 ms, duration 0.3 ms), and in the presence of 0.6 mbar of He as buffer gas. Curves corresponding to RF switched on and off are plotted, along with the signal

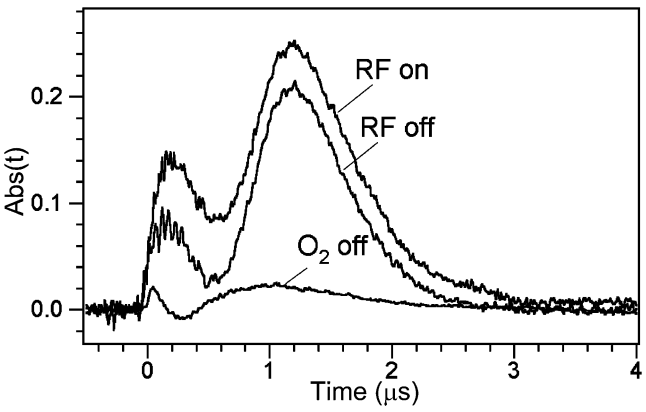

Fig. 2. Time-resolved absorption Abs(t) measured at $z = 6$ mm and $x = 0$ during PLD of a YBCO target at a fluence of 2 J/cm^2. The three curves correspond to different experimental conditions, as indicated in the plot. He buffer gas has been used, at the pressure of 0.6 mbar; delay and duration of the gas pulse were −2 and 0.3 ms, respectively.

acquired without O_2. Two distinct absorption features can be distinguished in the plots. The first peak, located a few hundreds of nanoseconds after the arrival of the ablating shot (the origin of the horizontal axis), is mainly due to residual plume emission collected by the photodiode, and is thus not representative of oxygen absorption. We note, however, that absorption by oxygen dissociated following collisions with prompt electrons [10] might contribute to the first peak, as well. The second peak reflects formation of atomic oxygen due to blast wave-driven dissociation of O_2. This peak is strongly suppressed when no oxygen gas is sent into the chamber, as seen in the figure, the residual absorption signal being due, in this case, to oxygen release from the target. At the distance from the target considered in the figure, the peak height is only slightly enhanced by the RF. Furthermore, it turns out to depend on the valve operating parameters. In particular, the delay plays an important role, and the maximum absorption is observed for a delay of a few milliseconds. Considering the length of the quartz pipe (180 mm) and the rise-time of the solenoid, such a finding suggests an average gas velocity below the supersonic speed. Finally, the presence of the buffer gas is another relevant parameter in our experiments. We found that He is particularly efficient in promoting O_2 dissociation, probably as a consequence of collisional-ionization and energy transfer processes involving high-level He states [15].

The behavior of the absorption as a function of the distance z from the target is shown in Fig. 3. As expected, the absorption peak shifts towards larger delays, and its height is reduced, for increasing distances, reflecting the decrease of particle density experienced by the plume during its expansion. Off axis measurements, i.e. obtained as a function of the x coordinate (Fig. 1), reveal that the transverse size of the oxygen

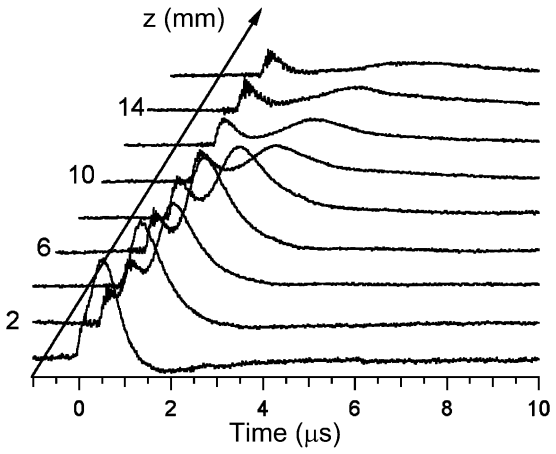

Fig. 3. Time-resolved absorption Abs(t) measured along the plume axis during PLD of a YBCO target at a fluence of 2 J/cm^2. Curves correspond to different distances z from the target, in the range 0–16 mm. He buffer gas has been used, at the pressure of 0.1 mbar and RF was switched on; operating parameters of the gas pulse as in Fig. 2.

absorbing region is 3–5 mm FWHM. No effects in the plume dynamics ascribed to mechanical interactions with the pulsed gas beam were observed.

We recall here that a primary goal of our investigations was to find the operating parameters able to reproduce in pulsed conditions the oxygen absorption found in conventional PLD experiments. To this aim, we have compared our data with those obtained with a continuous O_2 flow in the chamber, at a pressure of 0.3 mbar, that is the value typically adopted for the attainment of HTS YBCO films [11]. An example of the results is shown in Fig. 4a, displaying the height of the absorption peak as a function of the distance z from the target. The pulsed injection leads to a smaller peak absorption for distances up to 8–10 mm, whereas at larger distances practically coincident results are found. We note that in this case no buffer gas has been used in order to enable a better comparison. We recall also that the typical target to substrate distance used in YBCO film deposition is above 30 mm [11]. The average base pressure in the chamber, read with a vacuum gauge, was around one order of magnitude lower than for the continuous O_2 flow. Thus, we can conclude that the pulsed injection leads to a local density of atomic oxygen in the plume region not too smaller, or even comparable, to that achieved in continuous flow conditions.

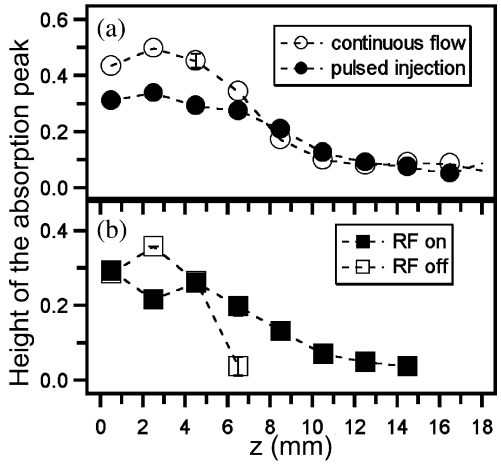

Fig. 4. (a) Comparison between the height of the absorption peak as a function of the distance z in continuous ($p(O_2)=0.3$ mbar) and pulsed flow conditions; in the latter case, no buffer gas was used; other parameters as in Fig. 3. (b) Comparison between the height of the absorption peak as a function of the distance z with RF on and off; He buffer gas was used at the pressure of 2 mbar; other parameters as in Fig. 3.

Finally, the role of the RF plasma is clarified in Fig. 4b, where the peak height is plotted as a function of the distance z from the target with or without the RF. Due to the relatively large He buffer gas pressure (2 mbar) used in the measurement, the plume range is rather small, as demonstrated by the sudden decrease of absorption at $z>6$ mm in data without RF. Nonetheless, at this buffer gas pressure, the RF excitation turns out efficient to promote O_2 dissociation even at relatively large distances from the target.

5. Conclusions

We have shown, through in situ diagnostics based on absorption spectroscopy, that synchronous pulsed injection of O_2 gas combined with RF plasma is a viable strategy to obtain a significant amount of atomic oxygen in the plume expansion region during PLD experiments. Such highly reactive species can combine with the metal materials ablated from ceramic targets to produce molecular oxides and oxidized clusters, whose arrival onto the target is expected to favor the attainment of the correct film stoichiometry.

Advantages with respect to conventional PLD of ceramics are in the reduced exposure of the sample to oxidizing agents, that can be a key point in the fabrication of coated conductors on flexible metal substrates.

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