

A reactive laser ablation source for the production of thin films

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A description of a thin film deposition source which is based upon the "Smalley metal cluster source" is presented. Our laser assisted molecular beam deposition source incorporates four major innovations: (1) placing the source so it sits external to the deposition chamber, (2) positioning the ablation target at an angle greater than 90° with respect to the laser entrance window, (3) placing the laser entrance window/lens further from the ablation target, and (4) the addition of a second optical window for laser alignment and *in situ* spectral analysis of the laser ablation plume. Novel molecules can be generated in this source through use of a reactive carrier gas. For example, employing a Ti target rod and O₂ carrier gas; flat, uniform micron thick thin films of TiO₂ can be easily generated. © 1998 American Institute of Physics. [S0034-6748(98)03908-2]

I. INTRODUCTION

The Smalley metal cluster source has had a long history of use for the generation of gas phase metallic clusters and the subsequent study of their physical and chemical properties.¹ In typical operation, the source sits within a vacuum chamber where a pulsed laser is used to create a hot plasma which ablates material from a target surface. A carrier gas is then used to entrain the ablated material via a cooling expansion through a molecular beam nozzle into the chamber. The expansion of the ablated material generates clusters in a wide distribution of sizes¹ and it is these species which can be employed in a variety of experiments. Much effort has been expended on modification of the original Smalley source to improve overall cluster yield and to produce more stable cluster beams.²⁻⁴ As one example, a recent modification of this source has been implemented to produce clusters of more than one metal in controlled ratios.⁵

While considerable research has been performed to improve the production of metal cluster beams, there has been far less work in the area of using this type of source to generate thin films. That is, can this source generate films of better quality in comparison to conventional pulsed laser deposition (PLD)?⁶⁻⁸ Using the Smalley source concept, the laser assisted molecular beam deposition (LAMBD) source has been developed for the sole purpose of thin film production. Some first efforts to deposit thin films have consisted of generating metal oxide thin films,⁹ organic guest/inorganic matrix composite films,^{10,11} copper embedded polymeric films,^{12,13} metal halide films,^{7,14} and other types of inorganic films such as SiC¹⁵ and CeO₂ on Si(111).¹⁶ In a past study, YBa₂Cu₃O_{7- δ} was deposited with the LAMBD source.⁶ The films were generated by ablation of a pure YBa₂Cu₃O_{7- δ} target and pulsing inert gas or inert gas mixed with oxygen. The films had a uniform morphology and analysis by energy

dispersive x-ray (EDX) and electron spectroscopy for chemical analysis (ESCA) were shown to have the proper stoichiometry, but the films were not superconducting, probably due to small amounts of an Al contaminant which was detected in analytical tests. Further work on superconducting films is currently in the planning stages.

II. EXPERIMENT

The LAMBD source sits external to the deposition/vacuum chamber. The source itself consists of an aluminum block which holds the axis of the 6.35 mm diam target rod in a fixed position relative to a commercial pulsed valve (General Valve Series 9). The valve is typically operated to produce a 1 ms gas pulse duration (as measured by a Beam Dynamics fast ion gauge) with a volume of 30 μ L at standard temperature and pressure. The target rod is continuously rotated and translated by a screw drive attached to a stepper motor. This drive indexes the target rod between every laser pulse, such that with each laser shot a fresh spot on the rod is ablated. A pulsed excimer laser beam (Lambda Physik EMG 150, 248 nm KrF, 200 mJ/pulse, 20 ns/pulse) is directed onto the target rod via a double lens focusing system. The energy reaching the source is controlled by an adjustable manual iris, from 5 mJ/pulse to 200 mJ/pulse, which adjusts the ablation conditions as required for different materials. The laser beam enters the source through a 25.4 mm diam laser entrance window and down a channel (4.5 cm long) into the source block to reach the laser target. The resulting ablation plasma plume is crossed by a synchronized gas pulse expanded from the pulsed valve's 1.5 mm diam nozzle. The gas enters the source directly across the ablation spot from a distance of 4 mm. The geometry of the source is shown by the cut away view in Fig. 1. The gas pulse is directed into the plane of the figure and out the orifice labeled expansion nozzle. The substrate sits behind and parallel to the plane of the figure. The gas pulse is tangent to the target rod and intersects the spot at which the laser beam impinges upon the

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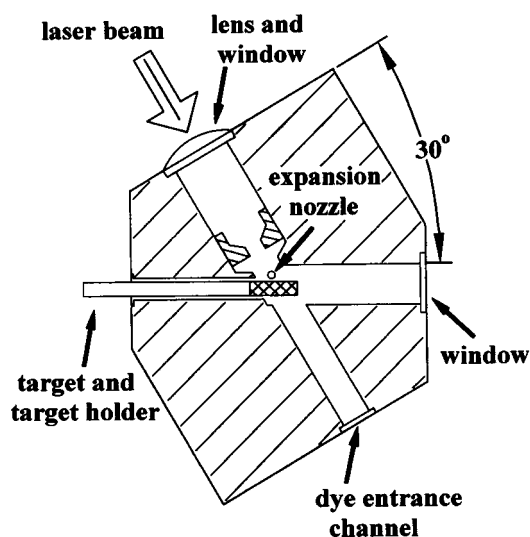


FIG. 1. Cut away view of the LAMBD source. Note when the ablation plume expands normal to the rod, it does not deposit directly upon the laser entrance window.

target. The gas can be either an inert buffer gas (such as He or Ar), or a reactive gas (such as O_2 or NH_3). An inert gas produces films of the pure target material, while a reactive gas will give reaction products such as oxides or nitrides of the target material. The resulting mixture of gas and ablation material expands out of an exit nozzle located in line with the pulsed valve entrance nozzle. The exit nozzle is located approximately 4 mm from the laser ablation spot and 8 mm from the pulsed valve entrance nozzle. After the exit nozzle, the expansion is directed into a 12.5 mm diam by 12.5 mm long cooling channel, and toward the substrate. In some experiments, a second pulsed valve is employed which introduces another molecular component (such as an organic laser dye) into a port in the source block, such that two substances are codeposited onto the substrate to create a composite film.^{10,11} The vacuum chamber is evacuated by an oil diffusion pump with a liquid nitrogen trap. The ultimate background pressure of the vacuum chamber is 1×10^6 Torr. The pressure in the chamber is typically set at an average value of 5×10^5 Torr during the film deposition.

Laser alignment, target rod replacement, and ablation plume monitoring are all simplified because of the LAMBD source's external design. Another advantage of having the source external to the vacuum chamber is the large aperture light channel. To achieve good clustering conditions in other beam sources, high pressure gas pulses (6 atm) are utilized.⁴ Narrow light channels (as small as 2 mm in diameter)² are therefore required in these sources to help maintain a favorable pressure differential between the source and the vacuum chamber. The light channel in the LAMBD source is 2 cm in diameter. This allows for easy laser alignment and short focal lengths. Not having the light channel open to the vacuum chamber in the LAMBD system also allows for the gas stagnation pressure to be as low as 4–10 psig for thin film production. In principle, this is a more economical use of the pulsed gas and a lower volume vacuum pumping system can be employed. One problem with our original source design

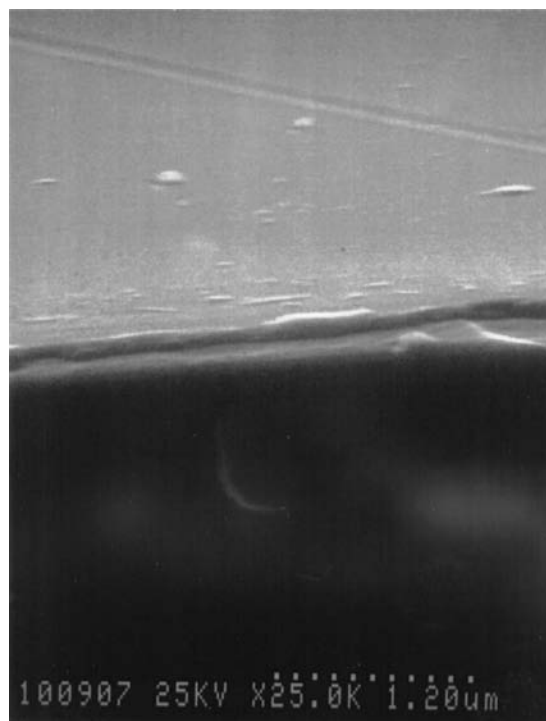


FIG. 2. SEM of TiO_2 film deposited by redesigned LAMBD source upon a room temperature glass substrate: 200 nm thick film 4.9 cm^2 , 150 mJ/pulse at 10 Hz, 72 000 laser pulses, 4 psi O_2 stagnation pressure.

(which will be referred to as **I**) was the long run times required to generate micron thick coatings. An additional difficulty for some target materials, such as Ti, was that the laser entrance window would rapidly coat with ablation material, attenuating the incoming laser beam and shutting the ablation process down.

III. RESULTS AND DISCUSSION

Shown in Fig. 2 is an scanning electron microscope (SEM) image of a 200 nm thick and 4.9 cm^2 TiO_2 film generated by our newly redesigned LAMBD source (from now on referred to as **II**) using a Ti target rod, pulsed O_2 carrier gas, and a glass substrate held at room temperature. Discounting the stressed area near the cleavage, only four sub-micron particles in an area of approximately $6 \mu\text{m}^2$ are visible. The line seen on the film is due to a scratch on the substrate prior to deposition. This TiO_2 was deposited by 72 000 pulses of a laser with a pulse energy of 150 mJ.

In one typical experiment using source **II**, 0.8 mg of material was ablated from a Si target rod (determined by mass loss from the target rod) with N_2 pulsed gas and 10 mJ/pulse energy with 38% of the ablation material being deposited upon the substrate (as determined by volume of the thin film and density of bulk Si).¹⁷ This film was deposited upon a Si(111) substrate held at room temperature using 72 000 laser pulses to produce a 100 nm thick uniform thin film with an area of approximately 7 cm^2 . The Si film surface was of comparable quality to that of the TiO_2 film.

Deposition rates are a relatively complex issue depending on ablation rates and the deposition geometry. The present 90° flow geometry, i.e., the ablation plume crossing

the gas pulses at 90°, is not optimized for maximum deposition rate, but rather to produce high quality films with low particle density. The deposition rate may be substantially increased, for example, by crossing at a smaller angle. It remains the subject of further studies as to whether this will produce films of comparable quality, or if there will be a trade off between film quality and the deposition rate. A similar trade off generally exists between laser pulse energy and deposition rate. The maximum usable laser pulse energy generally is dependent upon the material being ablated. Ti is difficult to ablate and further increases in the laser pulse energy would produce faster ablation and deposition rates and would probably still maintain the film quality. In contrast, increasing the laser pulse energy upon a Si target would increase particle density on the film.

Other design changes incorporated into **II** were made to minimize coating of the laser entrance window during the course of a deposition. After a TiO₂ film was deposited using source **I**, visual inspection of the laser entrance window revealed a uniform gray film produced upon the inside surface of the laser entrance window after only 20 min of 10 Hz operation. This deposition on the entrance window drastically reduced the laser radiation reaching the target, requiring longer deposition times and ultimately limiting the achievable thickness. In source **I** the target rod is parallel to the laser entrance window, that is, the laser beam is perpendicular to the target rod. When the target is ablated, the plume expands normal to the target¹⁸ and of course is preferentially directed towards the laser entrance window, rather than toward the exit nozzle. To alleviate the window coating problem a major design change for source **II** was to position the target rod 30° past parallel to the laser entrance window, as shown in Fig. 1. Material in a laser plume has been shown to follow a distribution of the general form: $D = \cos^p \Theta$ where D is the plume density and Θ is the observed polar angle of ejection from the target.¹⁹ For the ablation conditions in our system the value of p is around 8.¹⁹ With such a narrow distribution, the majority of the ablated material is directed towards the interior of the source, and then through the exit nozzle by the pulsed gas. With source **II**, much thicker TiO₂ films can be deposited because effective run times now can be 200 000 pulses or longer since the laser entrance window remains clear. This configuration has the additional advantage that macroscopic particles from the laser plume are captured within the source and are not deposited on the substrate as in conventional PLD.¹⁹ That is, only ‘‘small’’ atomic or molecular cluster species are swept by the gas pulse through the exit nozzle and onto the substrate when using the LAMB system. Smooth nearly droplet free thin films of TiO₂ can now be routinely produced using **II**.²⁰ (See Fig. 2.)

The third major design change was to move the laser entrance window 1.5 cm further away from the ablation plume than in **I**. Even though most of the ablation is not directed towards the window, there is turbulent mixing of the plume and expanded gas.¹¹ Placing the window further from the mixing region tends to reduce deposition on the laser entrance window.

The final modification to the source is the addition of a

19 mm diam quartz observation window on the source to optically monitor the ablation plume while the source is in use. The top viewing window facilitates focusing of the laser beam and permits spectroscopic monitoring of the laser plume. Emission spectra of the laser plume can also be recorded^{20,21} or a single emission line can be monitored to record changes in the ablation process over time.

In conclusion, we have found that by mounting the LAMB source external to the deposition chamber, changing the alignment of the target rod relative to the laser entrance window, moving the laser entrance window further from the target rod, and the addition of an observation window in the source, ease of operation and the quality of thin film production is greatly enhanced.

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