# Pulsed-laser deposition of smooth high-$T_c$ superconducting films using a synchronous velocity filter

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Pulsed-laser deposition of smooth high-$T_c$ superconducting films almost free from droplets and precipitates with the use of velocity filtration of plasma particles is reported. We have removed droplets from laser-induced plasma by using a shutter technique; a reduction of the droplet density by a factor of $10^5$ has been achieved. We have applied the technique to the preparation of high quality $YBa_2Cu_3O_{7-\delta}$ films on (100)-oriented $SrTiO_3$, MgO, $Y_2O_3$-stabilized $ZrO_2$ (YSZ) substrates and, furthermore, on $(1\bar{1}02)$-oriented sapphire covered with (100) sublayers of Si and (100) YSZ buffer layers. © *1995 American Institute of Physics.*

Dielectric,[1] semiconductor,[2] metallic,[3] or high-$T_c$[4,5] thin films prepared by present techniques of on-axis pulsed-laser deposition usually contain a large number of droplets and other macro particles. It has been shown[1,2] that the droplet density can in principle be reduced using mechanical shutter techniques; for a review see Ref. 6. However, it was suggested[6] that particle filtering by mechanical means was not a practical solution because of a low reduction of droplet concentration (of only an order of magnitude). In this letter we report on a study showing that the density of macroparticles on $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films prepared by pulsed-laser deposition can be reduced remarkably, at least by a factor of $10^5$, by using a mechanical shutter synchronized with the laser pulses.

The principle of the velocity filtration of laser-induced-plasma particles is shown in Fig. 1. The particles leaving the target with different velocities are separated by their time of flight. Fast particles reach the substrate while slow particles are retained by a shutter. We will show that the average velocity $v$ of molecular fragments ejected from the target is much larger than the velocity $v_d$ of droplets and that the separation is possible by using a rotating disk chopper as a shutter.

We deposited YBCO films and also buffer layers by use of excimer laser radiation (wavelength 308 nm, pulse duration 15 ns, repetition rate 8–25 Hz) focused on rotating disk-shaped targets to a pulse energy density of 10–20 J/cm$^2$. The films were prepared by ablation of Y–Ba–Cu–O ceramic targets, and 20–100 nm thick buffer layers were predeposited *in situ* using a yttria stabilized $ZrO_2$ (YSZ) target of pressed oxide powder annealed in oxygen at 1500 °C. The YBCO films were grown on (100)-oriented single-crystal substrates of $SrTiO_3$, YSZ, and MgO as well as on $(1\bar{1}02)$ cut $Al_2O_3$ substrates with a 0.5 $\mu$m thick epitaxial (100)-oriented sublayer of Si covered with (100) YSZ buffer layers. The buffer layers were prepared by a two-step method described in Ref. 7. The YBCO films were deposited in oxygen atmosphere at a pressure of 0.3 mbar. The substrates of $1\times1$ cm$^2$ size were placed 4.5 cm from the targets and were kept at a well-controlled temperature of 740–760 °C. The deposition rate was 0.025 nm/pulse.

We have inserted in the laser deposition apparatus, between target and substrate, a disk chopper with an opening of 2.5 cm diam at a distance of 6 cm from the disk center. The chopper was rotated by a motor (a two phase induction ac motor of 3 W power, model No. DID-3TA, a product of the Russian aviation industry) with a revolution speed of up to 500 Hz. The laser pulses were triggered by a phase-adjustable electronic device which synchronized the laser pulses with the disk rotation. The chopper made from 10 to 50 revolutions between two subsequent laser beam pulses.

For obtaining information about the velocities of the molecular fragments, we measured the spatial distribution of the plasma radiation intensity by a photodiode in the wavelength range of 0.5–1 $\mu$m. In the signal coming from different regions of the plasma [Fig. 2(a)] we found three characteristic peaks. At a time $t\simeq0.1$ $\mu$s after the laser pulse stray irradiation occurred immediately from a 2 mm region near the target. The signal of a very high intensity from this region we related to radiation of the originally excited target material. A second peak ($t\simeq2$ $\mu$s) reached its maximum over an area extending from 0.5 to 2 cm from the target. We relate this peak to the recombination of oxygen, which was excited most effectively at these distances by particles emitted from the target. While the two first peaks were observed almost at the same time (as stray radiation), there was a third peak of lower intensity which was distinguishable from the stray radiation at distances beyond 1.5 cm from the target. In time it moved with increasing distance from the target. We attribute this movement to a propagation of the plasma front and estimate the speed of the front to be about $5\times10^5$ cm/s. We conclude from our measurements that the plasma extended

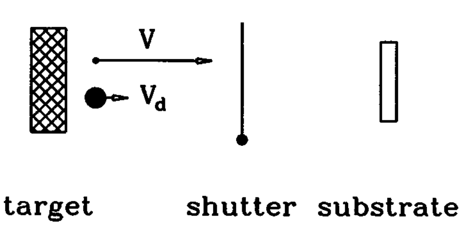


FIG. 1. Principle of velocity filtration of laser-induced plasma particles.

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over the whole target–substrate range during about 10 $\mu$s, together with decay of the plasma radiation.

However, the process of the laser-induced particle motion did not finish with the plume extinction. The oxygen needed for accomplishing the *in situ* YBCO film preparation process caused a very effective deceleration (thermalization) of the fast molecular fragments. To estimate the time interval in which the thermalized particles arrived at the substrate, we placed the chopper close to the substrate and adjusted the laser firing time to be earlier than when the disk opening passed the target–substrate line. We measured the thicknesses of the films produced with different phase delays of the disk opening. With zero delay the disk, when rotated with the revolution speed $f$ of 400 Hz shut the substrate in 80–100 $\mu$s and decreased the YBCO film mean deposition rate $D$ by a factor of 3. Reducing the rotation speed to 200 Hz we found that the deposition rate did not increase much. We suggested that a significant part of the YBCO material from the thermalized cloud near the substrate was depositing on the disk surface during a comparably long time. At nonzero delays it was possible to obtain high-quality YBCO films by depositing only the thermalized fragments with a reduced amount of droplets. The deposition rate change with the disk opening time delay was approximated (for $f$=400 Hz) by $D \sim \exp(-t/t_0)$, where $t_0$=230 $\mu$s. This formula characterizes the feed of the deposition region by the thermalized molecular fragments and allows an estimation of the cloud lifetime. About the same estimation was obtained with the use of a polished disk as the chopper. We found that after deposition of a YBCO film with $f$=400 Hz in the normal synchronized regime (i.e., without a delay) the disk placed near the substrate was covered on more than 1/4 of a turn with both the film and droplets. These experiments showed that the deposition process lasted about 0.5–1 ms after the laser pulses, and that the droplets came to the substrate nearly at the same time.

These time-of-flight measurements indicated that the

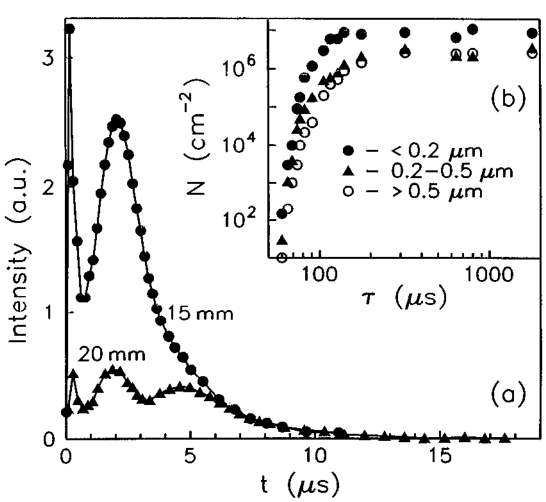


FIG. 2. (a) Time dependencies of the intensity of radiation of the laser-induced plasma at two distances from the YBCO target. (b) Densities of droplets of different sizes deposited together with 200 nm thick YBCO films prepared with different shutter delay times, and with a target chopper distance of 2 cm.

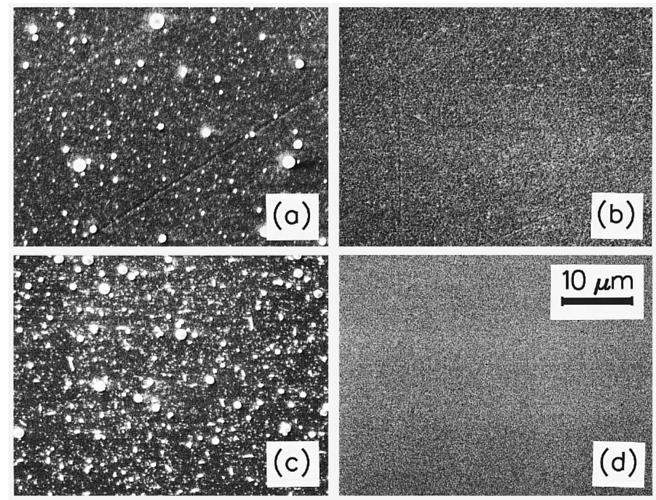


FIG. 3. Surfaces of YBCO films prepared on (100) oriented substrates of YSZ without (a) and with (b) velocity filtration and on MgO without (c) and with (d) filtration of the laser-induced plasma.

proper placing of the chopper between target and substrate was very important. As the average velocity of the molecular fragments decreased with distance from the target but that of the droplets was not much changed by passing through the gas, we chose a chopper position 2 cm from the target, i.e., at the region of the strongest deceleration of the plasma stream. In this configuration the main part of the stream passed the chopper window ballistically in a very short time (of the order of 10 $\mu$s) and the most effective velocity separation between the droplets and the molecular fragments was obtained. The chopper placed in this position did not noticeably change the plasma plume, and also the film deposition rate, even at the highest rotation speed.

To estimate the efficiency of the droplet trapping we measured the density of droplets arriving at the substrates; in this case we used, as substrates, highly polished silicon plates and to completely exclude formation of precipitates on the film surfaces, we reduced the deposition temperature to 500 °C. For different chopper rotation frequencies we counted the density of droplets deposited by 8000 pulses; we determined the shutter opening times $\tau$, taking into account the geometric dimensions. We found [Fig. 2(b)] a sharp onset of the particle density $N$ for $\tau \approx 50$ $\mu$s and a saturation of $N$ for $\tau \gtrsim 150$ $\mu$s. We estimated an average velocity of the droplets $v_d \approx 2 \times 10^4$ cm/s, and found that it was not much different for droplet diameters in a range of 0.1–1 $\mu$m. In our arrangement about half of the droplets arrived at the substrates at $f \approx 250$ Hz, but only about $10^{-5}$ at $f \gtrsim 460$ Hz. The same efficiency was reached for preparation (in vacuum at a pressure of $10^{-6}$–$10^{-3}$ mbar of the YSZ buffer layers.

We also made small changes to the Y–Ba–Cu–O target composition to improve stoichiometry of our films and to suppress formation of Cu-rich precipitates. We found that the films produced (both with and without the chopper) with targets of a composition $YBa_2Cu_{2.8}O_{7-\delta}$ had practically none or a very small amount of precipitates and better superconducting properties (for instance, the critical temperature was about 1 K higher) than those prepared with stoichiometrical targets; to avoid growth of the precipitates it was also impor-

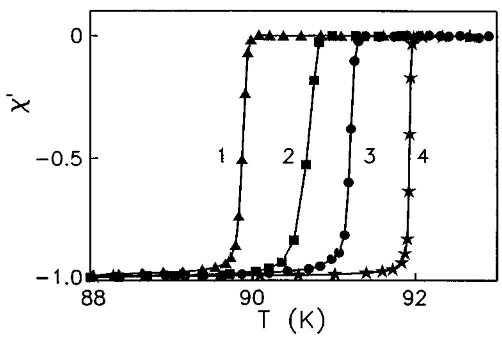


FIG. 4. Dynamic susceptibility $\chi'$ of droplet-free YBCO films prepared with velocity filtration on a $(1\bar{1}02)$ cut $Al_2O_3$ substrate covered with a (100) Si sublayer and a (100) YSZ buffer layer (1), and on (100)-oriented substrates of MgO (2), $SrTiO_3$ (3), and YSZ (4).

tant that the visible plume, containing the fast particles, did not touch the growing film surface.

The method of pulseld-laser deposition with velocity filtration of plasma particles allowed us to produce high-quality YBCO films with smooth surfaces. Samples of 200 nm thick films studied by electron microscopy are shown in Fig. 3. YBCO films on YSZ showed a large amount of droplets in case of no velocity filtration [Fig. 3(a)]. The number of droplets was very low if filtration was used [Fig. 3(b)]. Similar results were found for YBCO on MgO [Figs. 3(c) and 3(d)]. There were no droplets of $\gtrsim 1$ $\mu$m size and the density of smaller droplets usually was not more than $10^3$ $cm^{-2}$.

Figure 4 shows sharp alternating-field screening curves of the films deposited on different substrates with velocity filtration of the laser-induced streams and with the modified composition of Y–Ba–Cu–O targets. Zero resistance in these films was reached at $T_c$ $(R=0)=90.3$ K (1), 91 K (2), 91.4 K (3), and 92 K (4). As an example, the curve 1 in Fig. 4 belongs to a 112 nm thick film which for the first time was grown on a sapphire substrate with a Si sublayer and a YSZ buffer layer on the top. This film had a resistivity of 60 $\mu\Omega$ cm at 100 K and a critical current density, measured in a 42 $\mu$m wide bridge (using the criteria of 10 $\mu$V/mm), $J_c \simeq 3\times 10^6$ A/cm$^2$ at 77 K. These values are nearly the same as those measured in the best YBCO films deposited on Si with buffer layers to date.[6] X-ray diffraction measurements showed that all the YBCO films were highly (001)-oriented and single phase.

In conclusion, we have investigated the time of flight of both fast and thermalized components of laser-induced plasma, as well as droplets and other macroparticles ejected from the targets. Our experiments have shown that use of a fast shutter for velocity filtration of a laser-induced particle stream is an effective and convenient method of protecting a substrate from being hit by droplets. The droplet reduction we have reached is at least as large as that obtained by off-axis laser deposition[8] and by a method of intersected laser-induced plasma streams.[9,10] We have also found that a small reduction of Cu in the target composition from the stoichiometry suppresses the creation of precipitates on the film surfaces and improves the superconducting properties of the YBCO films. Using the technique developed, smooth YBCO films with $T_c$ $(R=0)=90.3$ K and $J_c \simeq 3\times 10^6$ A/cm$^2$ at 77 K on sapphire substrates with Si sublayers and YSZ buffer layers as well as high-quality YBCO films on other substrates have been grown.

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