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Influence of Pulse Width and Target Density on Pulsed Laser Deposition of Thin YBaCuO Film

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DISCLAIMER

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Abstract

We have studied the effects of temporal pulse width and target density on the deposition of thin films of YBaCuO. A 248nm excimer laser and an 825nm Ti-sapphire laser were used to conduct the experiments with pulse widths of 27 ns, 16 ns, and 150 fs, and target densities of 80% and 90%. Scanning electron microscope photomicrographs and profilometer traces show a striking difference between nanosecond and femtosecond laser irradiation. Shortening the pulse width reduced particulate formation, provided stoichiometry, and improved the film properties. Decreasing the target density raised the ablation rate, produced thicker but nonuniform films, and reduced particulate formation.

Introduction

Pulsed laser deposition (PLD) has been widely used for the deposition of high-critical-temperature (T_c) superconducting thin films and is recognized as a high-quality vapor-deposition technique for the preparation of films. The process of forming thin films through laser irradiation has been researched extensively over the last 20 years. High T_c superconducting thin films are being used in computer switches and in microwave components such as resonators and band-pass filters.[1]

The most important advantages of the PLD technique are (a) multilayered film can be deposited, (b) the films can have the same composition as the target, and (c) the deposition rate is faster than that of other techniques.[2] In most of the work on thin film deposition, high-T_c superconductors are used as the target material.

Wu et al.[3] proposed a number of Cu-based oxide superconducting thin films that are superconducting above 77 K. In most applications (e.g., microwave components), the films must have a high superconducting critical temperature. So far, the highest transition temperature obtained is 125 K in single-phase Tl-based oxide superconducting thin films.[3]

However, depositing these single-phase superconducting thin films of Tl-based oxides is very difficult. The alternative choice of superconducting material with a higher T_c is the well-

known 123 superconductor (YBaCuO), which has a transition temperature of 90 K. Extensive research has been conducted on 123 materials, and researchers have obtained a critical current density of 5 x 10^6 A/cm^2 at 77 K.[4] This is the highest ever achieved, and for this reason we chose YBaCuO as the target.

In this work, we have studied the roles of pulse width and target density (the two key process parameters that have not received full attention from the laser-processing community) in the deposition of thin YBaCuO films on Ni and Si substrates. Three pulse widths (27 ns, 16 ns, and 150 fs) were investigated, and target densities of 80% and 90% were examined. Advances in ultra-short-pulse, high-energy Ti-sapphire lasers allowed us to study the deposition process in much shorter time periods.

Experimental Setup and Measurements

A stainless steel vacuum chamber was designed by using Pro-Engineer software. The chamber contained five ports: substrate, target, laser, gas, and a viewing port. Each port was closed with a flange cover and an O-ring coated with vacuum grease to maintain the vacuum inside the chamber. A schematic diagram of the vacuum chamber is shown in Fig. 1.

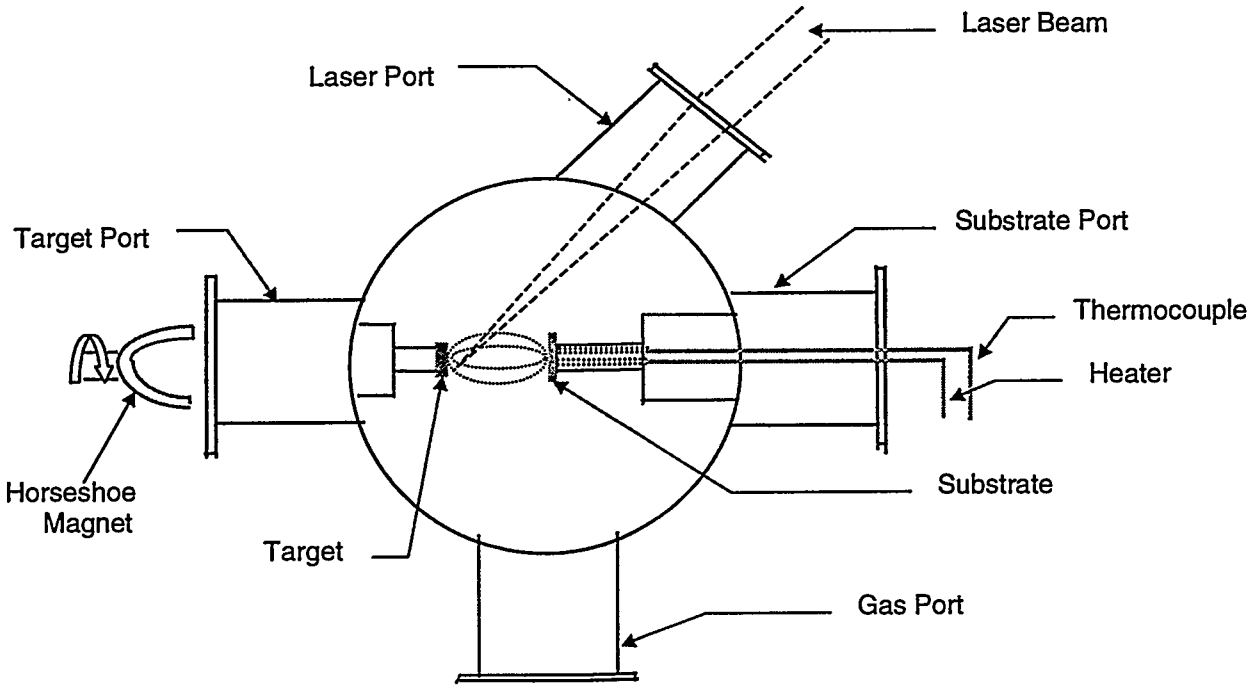

Fig. 1. Schematic diagram of vacuum chamber.

The laser port was positioned at an angle of 45° to the target port. The target was a disc of 25.4mm diameter and 3mm thickness and was secured with a silver paint glue that has a high working temperature range. A polymeric rod served as the target holder, which was rotated by an external magnetic field at the slow speed of ≈ 30r/min. This was done to achieve a uniform

ablation on the target surface. The target was rotated to allow considerable overlap with the previous area, causing any surface inhomogeneities to be averaged out.

The substrate was placed parallel to the target, and the substrate surface was ultrasonically cleaned with acetone. The distance between the target and substrate was varied from 20 to 60 mm. The substrate was heated to 450°C by a cartridge heater (15.2mm dia, 38mm length, and watt density of 75 W/mm^2). Substrate temperature was measured by a thermocouple, which, along with the heater, was inserted in the substrate holder. Oxygen at the required pressure was passed through the gas port.

Determination of T_c

The sample was sandwiched between two small electromagnetic coils, a primary coil and a secondary coil. Calibrated currents as high as 0.2 A, and frequencies to 50 kHz, were fed to the primary coil. Voltage induced in the secondary coil was detected and plotted directly against sample temperature. At room temperature, the secondary coil detected the flux from the primary coil with little screening. When the film superconducted, it screened the field and the mutual inductance, nominally dropping the voltage across the secondary coil to zero. We found that if inhomogeneities were present in the sample, if the transition to the superconducting state were gradual, or if two different superconducting phases were present in the sample, the flux would penetrate the film at a temperature below the critical value.[5]

Determination of Critical Current Density

Figure 2 shows a typical mutual inductance signal (voltage across the secondary coil) plotted against drive current in the primary coil. The temperature is below T_c. A lock-in amplifier is used to measure the voltage in the secondary coil. The in-phase component is proportional to the drive amplitude at low drive currents and becomes nonlinear at the onset of criticality. The out-of phase component (due to attenuation) is zero at low drive currents and deviates from zero

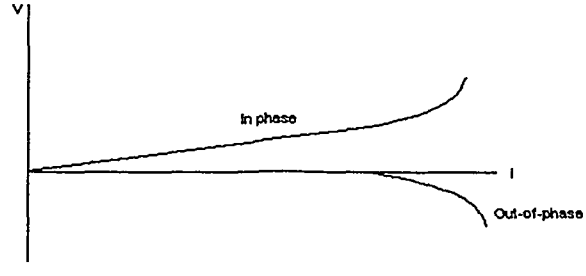

Fig. 2. Mutual inductance signal plotted against drive current.

at the onset of criticality. Available full-scale drive currents range from 0.2 mA to 0.2 A and produce full-scale normal drive fields nominally from 170 mG to 170 G (assuming a distance of 0.075 mm between the film and the surface of the primary coil mounting cylinder). At this geometry, the maximum tangential drive field is about 85 G at the superconductor surface, which

induces a sheet current density of 135 A/cm^2. In a 400nm thick film, this corresponds to a volume current density of 3.4 x 10^6 A/cm^2 (see Ref.5).

Experimental Procedure

The chamber was evacuated to 10^{-6} torr by a diffusion pump, the diffusion pump valve was then closed, and oxygen was passed into the deposition chamber through the gas port. Oxygen pressure was maintained at 20 mtorr by turning on the mechanical pump alone. The oxygen introduced into the laser plume was found to enhance the interaction and deposition that led to the formation of the desired superconducting phase. The 248nm excimer laser beam, with a beam size of 22 x 7 mm, was fired on the target at an angle of 45° to the target surface. Before hitting the target, the beam passed through a plano-convex lens (152.4mm focal length) to obtain a spot size of 5 x 1 mm on the target surface. The target was positioned so that the beam struck the target surface slightly away from the center, exposing it to a larger area for ablation.

The surface temperature of the YBaCuO target during the pulsed excimer laser irradiation was estimated to be ≈ 2000-3200 K.[6] At these high surface temperatures, appreciable fluxes of positive ions and electrons were produced, and target ablation was accompanied by a brilliant glow (laser plasma) extending outward from the surface. A photograph of the plasma generated by the excimer laser irradiation on the YBaCuO target is shown in Fig.3.

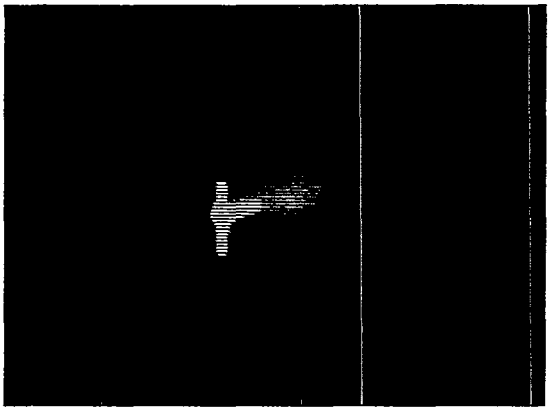

Fig. 3. Photograph of laser induced plasma generated by laser irradiation of YBaCuO target.

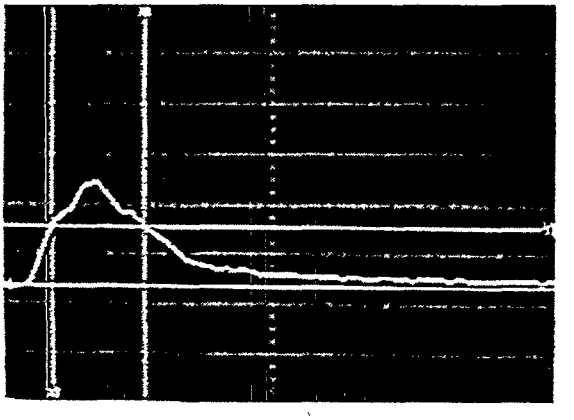

Fig. 4. Temporal profile of pulse obtained from digital oscilloscope.

Pulse energy of the laser beam was measured by a joulemeter (Gentec ED 200) connected to a digital oscilloscope. A photodiode was also connected to the oscilloscope to measure the pulse width. Figure 4 shows the temporal profile of a pulse (16 ns) obtained from the digital oscilloscope. The energy was 200 mJ. The samples were exposed to 3000 pulses at 1 Hz frequency, and the pulse width was varied between 27 and 16 ns. Lee et al.[6] reported that YBaCuO thin films deposited below 500°C are amorphous, and nonsuperconducting, and require postannealing in oxygen at high temperatures to attain their superconducting properties. Therefore samples were postannealed after deposition at 900°C in an oxygen atmosphere.

Results and Discussion

Nanosecond Pulsed Laser Deposition

The thickness of the film deposited on the substrate was measured with a profilometer (Solan Dektak II) set to scan 5 mm of the deposited surface. The average thickness was 3000A which amounts to about 1 A film per pulse(see Figs. 5a and 5b). For the sample deposited in the oxygen atmosphere (Fig. 5a), the film thickness was approximately uniform. But for the sample under vacuum, deposition was not uniform (Fig. 5b). Here, the thickness at some locations reached as high as 50,000 A. However, this could have been caused by foreign particles on the substrate surface. Both samples were initially placed 30 mm from the target surface. As target/substrate distance was increased to 65 mm, film thickness decreased.

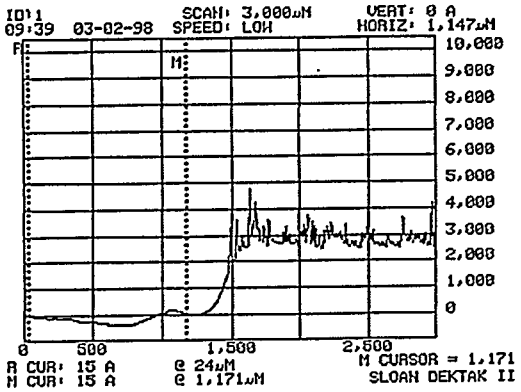

Fig. 5a. Profilometer traces of film thickness on silicon in oxygen atmosphere.

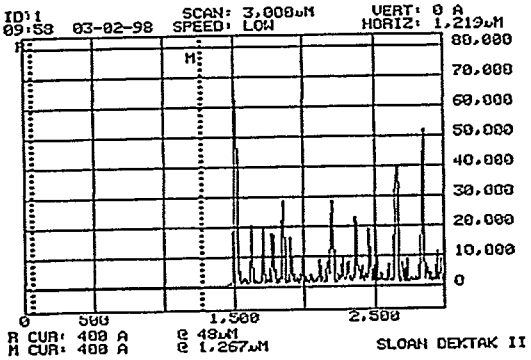

Fig. 5b. Profilometer traces of film thickness on silicon under vacuum.

Scanning electron microscopy (SEM) in conjunction with an energy-dispersive X-ray microprobe was used to analyze film particulates and composition. The particulates were

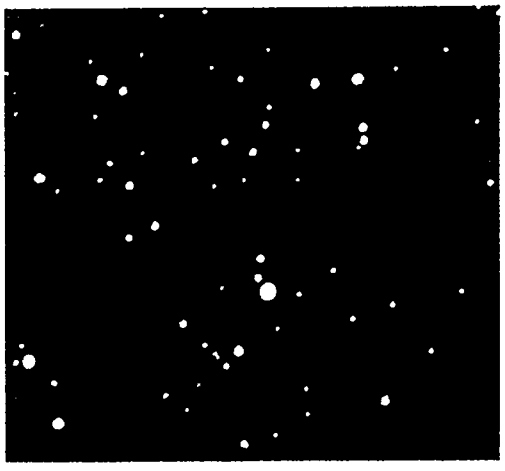

Fig. 6a. SEM photomicrograph showing particulates formed with pulse width of 27ns.

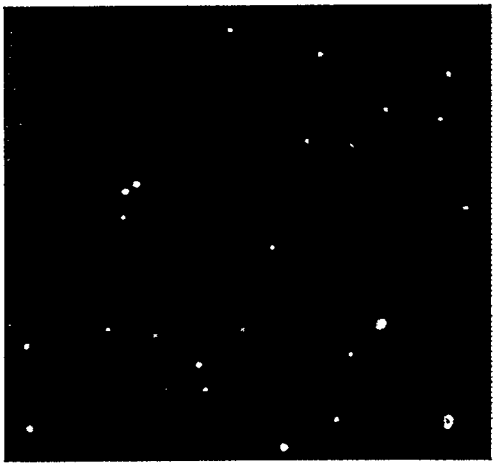

Fig. 6b. SEM photomicrograph showing particulates formed with pulse width of 16ns.

scattered in all the samples. Figure 6a is an SEM photomicrograph of particulates deposited on the substrate with the standard pulse width of 27 ns. Figure 6b shows particulates deposited on the substrate with a shorter pulse width of 16 ns. Both films were deposited under an oxygen atmosphere (20 mtorr) at a distance of 30 mm from the target. It is clear that the amount of particulates deposited with standard pulse width is much higher than that with the of 16ns pulses. A higher-density target was used in both cases. The lower-density target resulted in more particulate formation, as is seen clearly in Figs. 7a and 7b. Figures 8a and 8b show compositions of thin films deposited with 27ns and 16ns pulses, respectively. Pulse width seems to have a negligible effect on the composition. Y, Ba, Cu, and O were identified on the film, because the substrate was nickel, its presence was also detected.

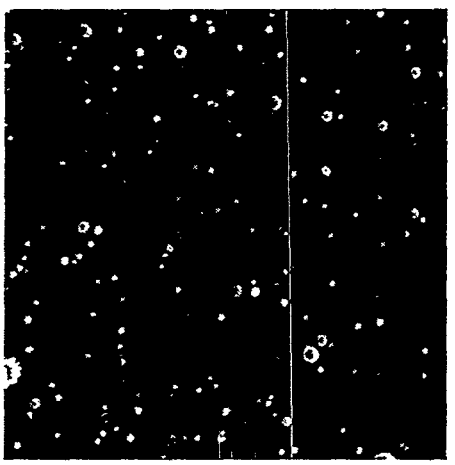

Fig. 7a. SEM photomicrograph showing particulates formed with 80% density target.

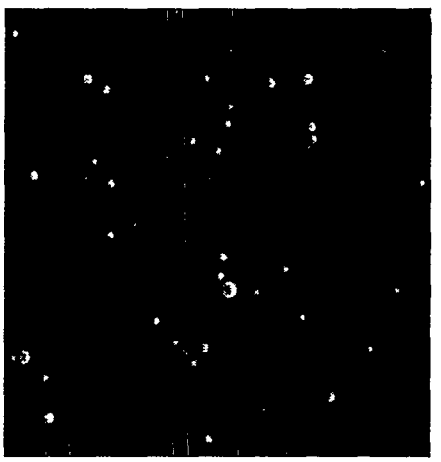

Fig. 7b. SEM photomicrograph showing particulates formed with 90% density target.

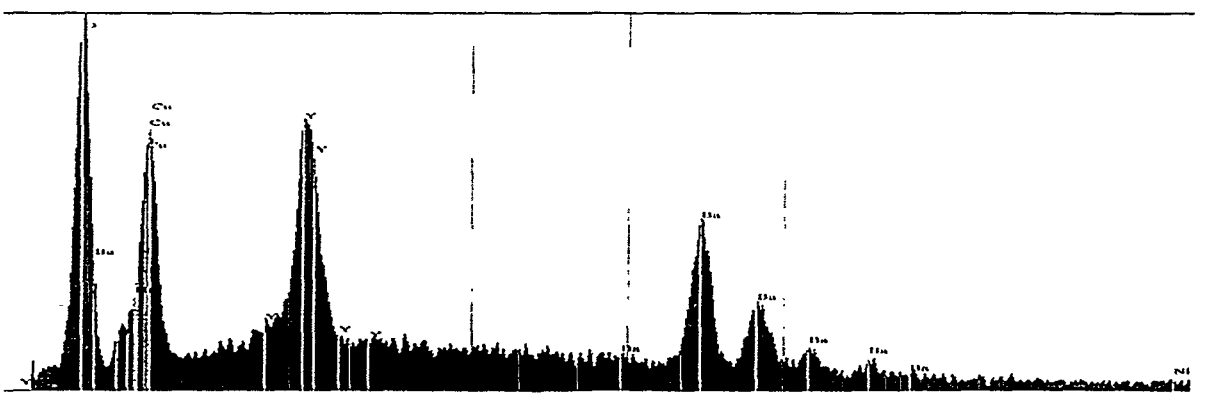

Fig. 8a. Energy-dispersive X-ray spectrum of composition of deposited film with 27 ns pulse.

Element	Atomic
O	84.379
Ni	0.351
Cu	1.116
Y	7.397
Ba	6.757

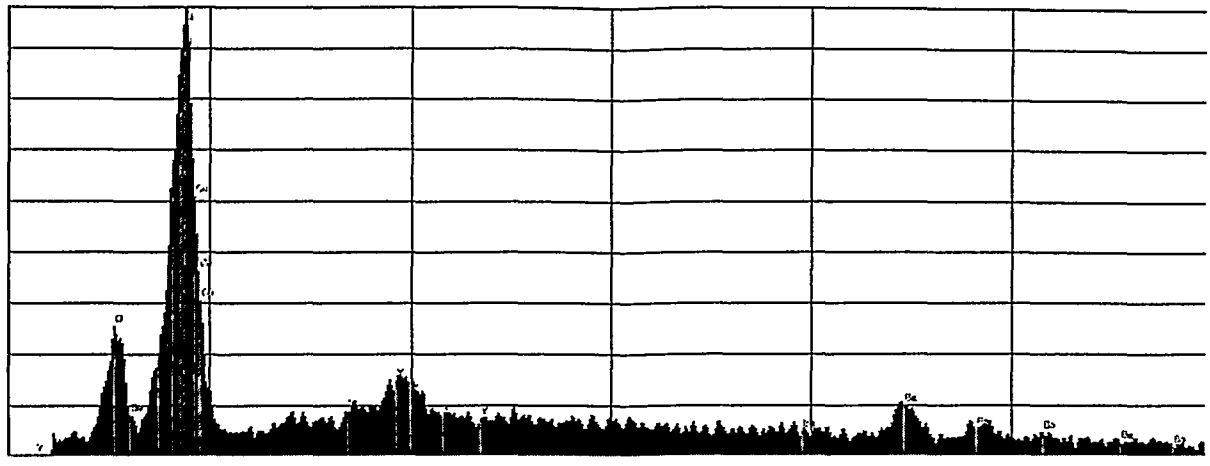

Fig. 8b. Energy-dispersive X-ray spectrum of composition of deposited film with 16 ns pulse.

Element	Atomic
O	84.916
Ni	0.252
Cu	0.965
Y	7.297
Ba	6.569

The films deposited with 27 and 16 ns did not yield high T_c and J_c values. This may be because the samples were annealed at very high temperature. According to Wu et al.,[3] high-temperature postannealing creates several problems: (a) Chemical reaction with the substrate that results in formation of a dead layer at the interface. (b) loss of film stoichiometry after annealing due to surface evaporation and film surface interaction. (c) crack formation during thermal cycling resulting in destruction of the percolation path for superconductivity in the film. and (d) roughing during thermal cycling, resulting in low critical current densities [7].

Femtosecond Pulsed Laser Deposition

After evaluating substrates deposited under 27 and 16 ns pulse widths, we inferred that better results could be obtained by higher-density targets and lower pulse widths. An attempt was then made to deposit films with a lower pulse width in the femtosecond range. A 825 nm Ti–sapphire laser was used for this purpose. The pulse width was 150 fs, with a repetition rate of 1 kHz. Deposition was performed at room temperature. Other laser parameters were marginally changed from those used in the nanosecond deposition. The experiment was performed under oxygen pressure of 20 mtorr throughout the deposition. The distance between the target and the substrate was 20 mm. A film thickness of ≈15000 A was obtained during a deposition period of 4 min and with a pulse energy of 2 mJ/pulse. Figure 9 clearly shows the film thickness obtained using the femtosecond laser pulse width. Here, film thickness is very high and approximately uniform when compared with the nanosecond pulsed laser deposition. At one location, the thickness is as high as 31,000 A, possibly because of foreign particles. Figure 10 is an SEM photomicrograph of particulates deposited on the substrate with the femtosecond pulse width of 150 fs. No particulates were observed, but it has a coarse surface when compared to the ns pulses.

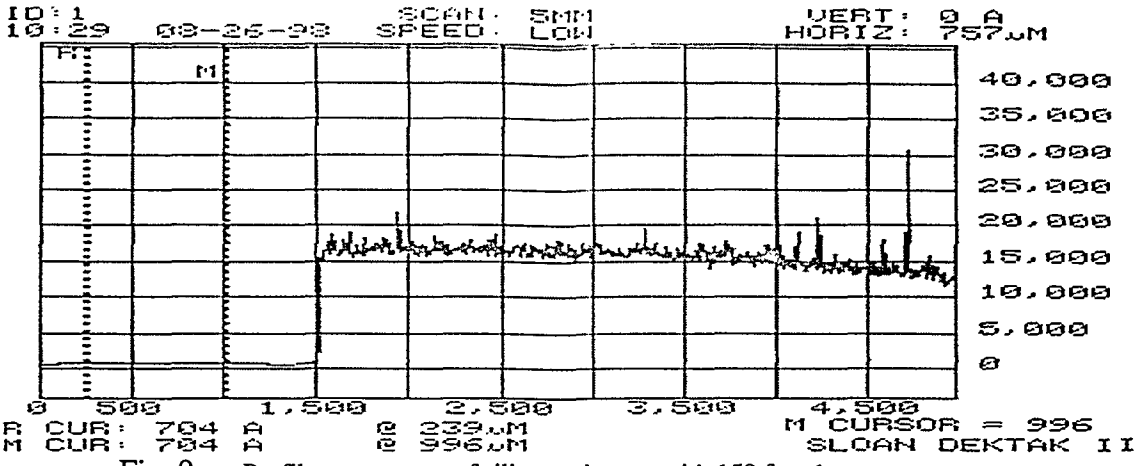

Fig. 9. Profilometer traces of silicon substrate with 150 fs pulses.

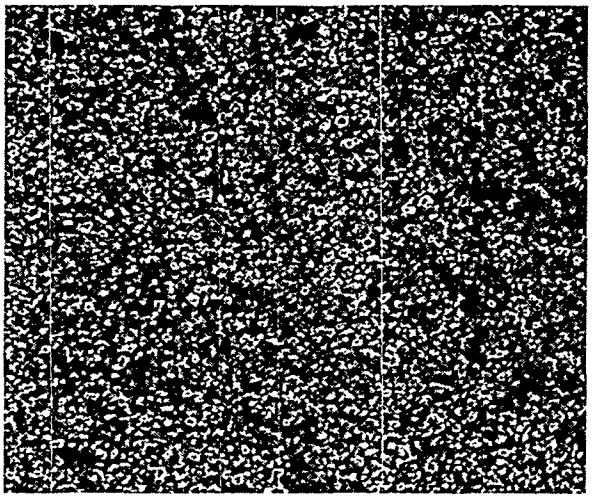

Fig. 10. SEM micrograph showing the particulate formation with fs pulses

Because high-temperature postannealing resulted in low film quality, the samples deposited under femtosecond pulses were annealed at 450°C for 3 h in an oxygen atmosphere of 20 mtorr. We found that the T_c and critical current density values for the film deposited via femtosecond pulse width were much higher than those for the films deposited in 27 and 16 ns. Because of postannealing, the film thickness was reduced. Figures 11a and 11b shows a bright-field image of the YBaCuO layer on silicon with ns and fs pulses. A thin (≈10 nm) amorphous layer is also visible between the YBaCuO and the silicon in both the cases.

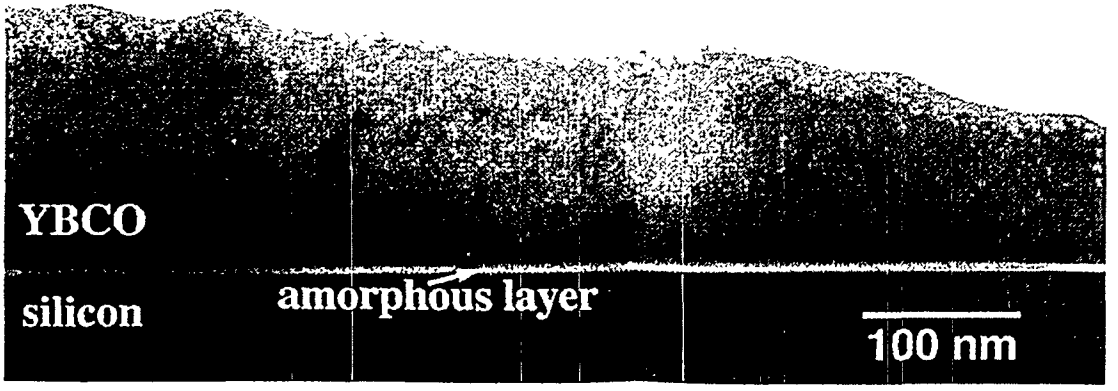

Fig. 11a.

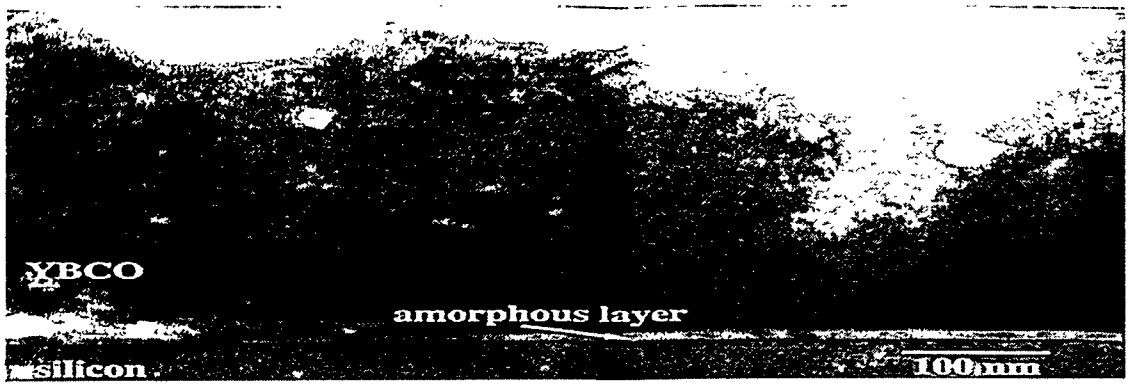

Fig. 11b.
Field image of YBaCuO with ns pulses(Fig. 11a.), fs pulses(Fig. 11b.).

Figure 12 shows a selected area diffraction pattern (SAD) from the YBaCuO layer. A few possible areas of texturing are apparent, but the image also exhibits some features that correspond to a random polycrystalline layer.

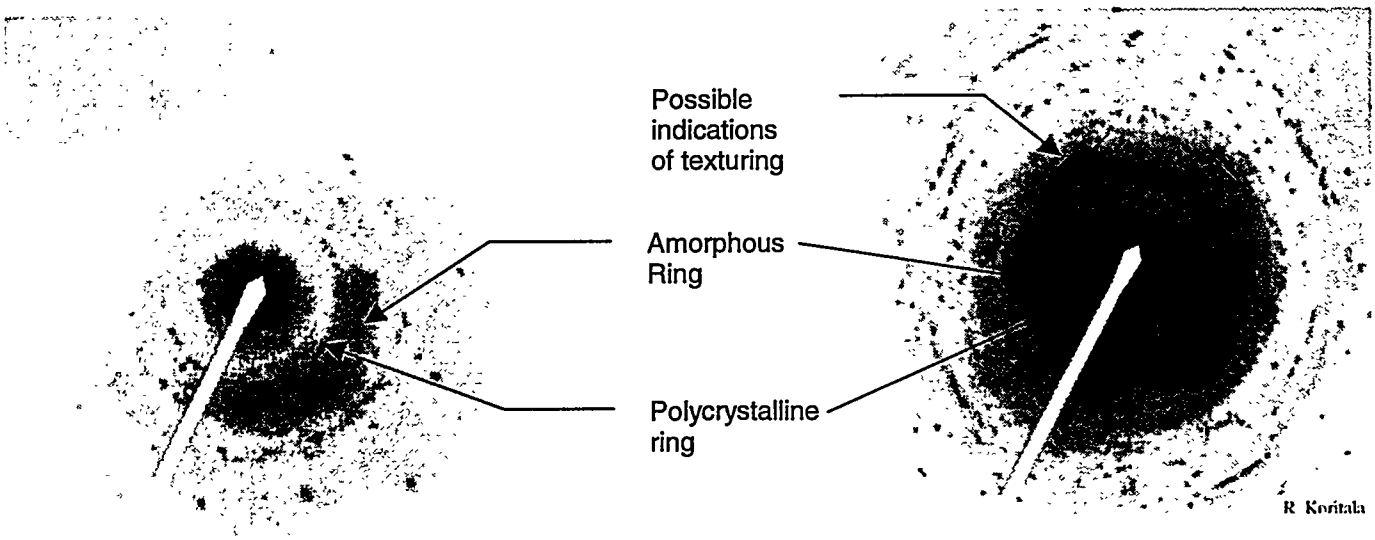

Fig. 12. Selected area diffraction pattern (SAD) from YBaCuO layer.

Conclusions

We have studied laser ablation and subsequent film deposition of YBaCuO with an excimer laser at pulse widths of 27 and 16 ns, and also with a Ti-sapphire laser at a pulse width of 150 fs. The microstructure and quality of the deposited film depends not only on pulse duration but also on target density. We have shown that femtosecond laser pulses are particularly effective in depositing high-quality YBaCuO thin films. This is attributed to the high kinetic energies obtained in the plasma and to the formation of only small particulates. Femtosecond-pulsed lasers offer promise for growing quality films in pulsed laser deposition.

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Dr. R. E. Koritala is a postdoctoral appointee at Argonne National Laboratory and specializes in the transmission electron microscopy of ceramic materials. Her areas of interest include superconductors, thin films, and composites. Her supervisor is Dr. U. Balachandran, manager of the Ceramics Section at Argonne National Laboratory. His areas of research include superconductors, fuel cells, and ceramic membranes.