LA-UR 91-3463

LA-UR--91-3463

DE92 002518

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

TITLE: LASER DEPOSITION AND LASER MODIFICATION OF HIGH-TEMPERATURE SUPERCONDUCTING THIN FILMS

AUTHOR(S): R. C. Dye, S. R. Foltyn, N. S. Nogar, X. D. Wu, E. J. Peterson, and R. E. Muenchausen

SUBMITTED TO: Proceedings of Electrochemistry Society meeting, Phoenix, AZ, October 13-17, 1991

DISCLAIMER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

LASER DEPOSITION AND LASER MODIFICATION OF HIGH-TEMPERATURE SUPERCONDUCTING THIN FILMS

R. C. Dye, S.R. Foltyn and N. S. Nogar
Chemical and Laser Sciences Division

X. D. Wu and E.J. Peterson R. E. Muenchausen
Exploratory Research and Development Center
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

Applications of high-temperature superconductors (HTSC) may require epitaxial thin films with $T_c \geq 77$ K, and $J_c \geq 10^6$ A/cm^2. *In-situ* pulsed laser deposition (PLD) is suitable for fabrication of such films. We report parametric studies on the effect of laser and processing parameters on the crystallinity, epitaxy and electrical properties of laser-deposited HTSC thin films.

In addition, several laser-based processes were used to modify the electrical properties (T_c and J_c) of PLD thin films. A direct-write laser heating (1.06 μm at ≈0.5 kW/cm^2 for ≈5 min) process in an oxygen atmosphere at ≈590 Torr was shown to selectively regenerate high-T_c material in microscopic domains from films that were partially deoxygenated. In separate work, electrical responses and crystallinity of HTSC films were measured as a function of excimer laser exposure using fluences in the rang 20-150 mJ/cm^2. The critical current and boundary layer could be modified with a high degree of accuracy.

1. INTRODUCTION

Many microelectronics, microwave and optoelectronics applications of the new metal-oxide based high-temperature superconductors (HTSC) will require epitaxial (high J_c) thin films with transition temperatures, $T_c \geq 77$ K. *In-situ* pulsed laser deposition (PLD) offers considerable promise for the fabrication of such films, even over large areas, in addition to buffer-layer and multilayer coatings [1-5].

Potential device structures for high-temperature superconducting (HTSC) thin films include interconnects, oscillators, switches, junctions, SQUIDs, filters and delay lines [6]. All applications will require the generation (and possible erasure) of superconducting structures in well-defined domains, preferably under gentle processing conditions. Critical current control may also be

required for some applications. Mild processing conditions with an exceptionally clean interface between the superconducting and non-superconducting regions may be necessary to produce high quality HTSC thin-film devices. Several lithographic and direct-write patterning techniques, including ion-milling, plasma-etching, and wet chemical etching have been reported. These techniques may produce a damaged boundary or layer at the interface between the original high-T_c and modified materials that can severely degrade device performance.

We describe in this manuscript major characteristics of the laser deposition process for $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductors, including characteristics of the laser generated plume, and modifications occuring on the target surface. In addition, several methods for pattering of HTSC thin films, and for the modification of both T_c and J_c under relatively mild processing conditions, are described.

2. EXPERIMENTAL

The apparatus developed for PLD of YBCO thin films[7] consists of a modified six way 6" dia. stainless steel cross as shown in Figure 1. Load locks are provided for target and substrate introduction to minimize pumping times. The target can be rotated in conjunction with horizontal rastering of the laser beam while the substrate can be rotated to ensure uniform thickness (±10%) across the substrate diameter. The exposure (shots/site) was calculated by simply dividing the number of shots by a geometrical factor which is the area ratio of the annular ring of target material exposed divided by the laser beam area. Tilt flanges (±2°) allowed for precise alignment of target and substrate.

Provisions were made to heat the substrate, either indirectly on a Ni block or radiatively[8]. Deposition rates were measured by substituting a Inficon XTC, quartz microbalance (QCM) at the substrate position. Measured thickness values were calibrated by Rutherford backscattering (RBS) measurements. Processing gases were introduced into the deposition chamber using mass flow control to maintain a constant pressure. The excimer laser used in these experiments (Lambda Physik 203EMG) produced 200 mJ, 20 nsec pulses at 308 nm at repetition rates typically around 10 Hz.

Additionally, for some of the experiments described here, the plume optical emission was collected and analyzed[9]. One of two methods was used, depending on whether spatial or spectral resolution was required. In the former case, emission from the plume was passed through a narrow-band (≈2 nm) interference filter, collected by a compound lens, and focussed onto a gated, intensified CCD detector. This allowed spatially resolved measurements, with a temporal resolution of ≈25 nsec. In the latter case, light was collected by a 7.5 cm. diameter, 500 cm focal length quartz lens, and focussed onto the end of a (200 μm diameter) multi-mode fiber optic cable (FOC), 10 m in length. The

distal end of the fiber optic cable was coupled to an 0.5 m monochromator equipped the CCD camera for spectrally resolved detection.

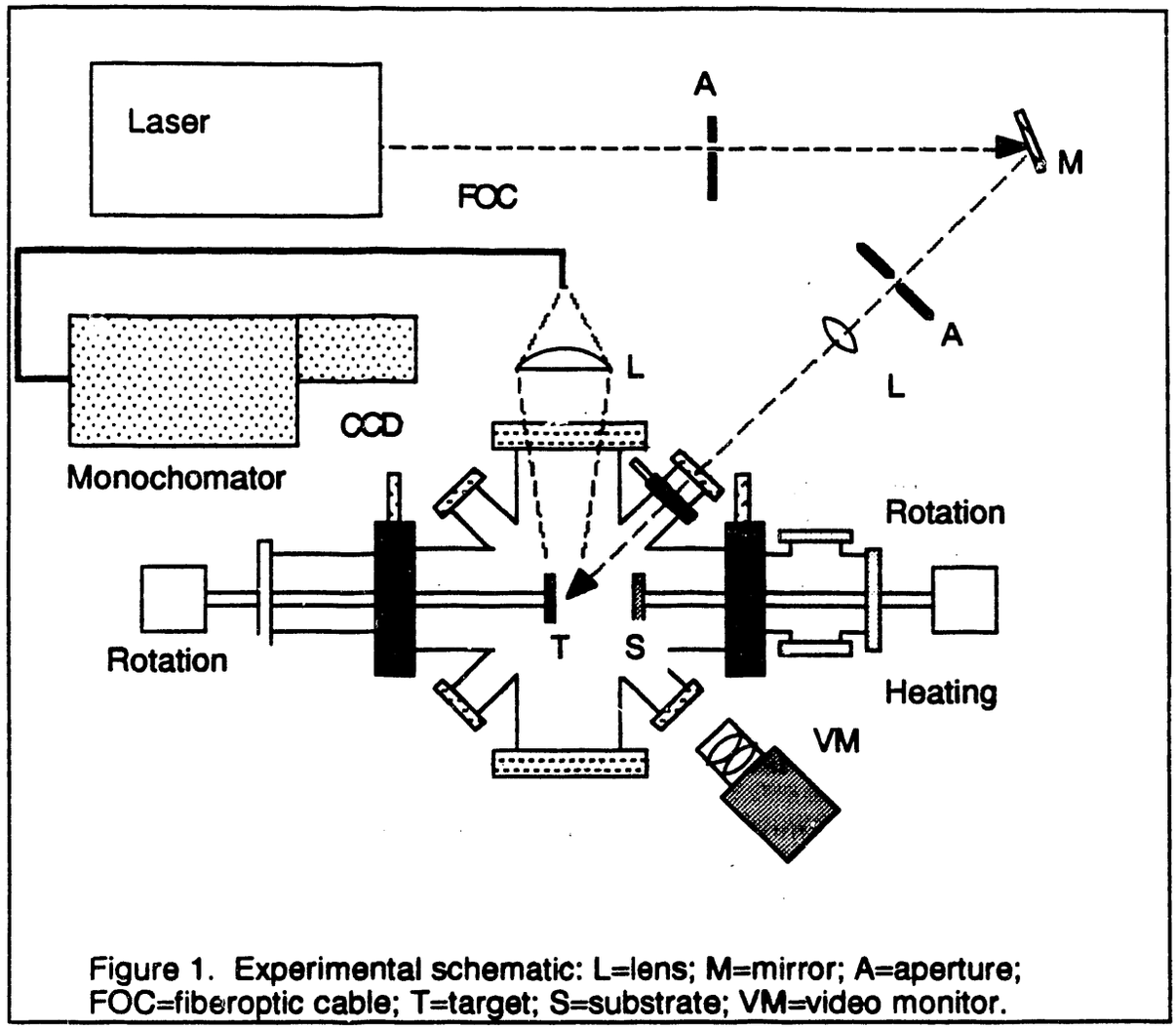

Figure 1. Experimental schematic: L=lens; M=mirror; A=aperture; FOC=fiberoptic cable; T=target; S=substrate; VM=video monitor.

For experiments in laser writing, the thin films, after thermally annealing the films in an argon atmosphere at a temperature of 400° C for 5-20 minutes, exhibited either no superconducting transition, or a transition temperature less than 60 K due to oxygen loss. Selected areas of the depleted film were then regenerated to 90 K by placing the sample in an oxygen chamber and radiating with 1.06 μm light from a Nd^{+3}:YAG laser operating at 80 MHz to produce 3.5 W of output. The beam was focused to approximately 0.5 mm^2. Patterns were established by having the sample in a windowed chamber which was mounted on a programmable, X-Y translational stage. The rate of travel of the stage was varied in the range near 0.1 mm/min. The patterns were then characterized by four-point probe and rf-eddy current measurements, as well as optical and electron spectroscopies.

The experiments on critical current modification used a simple contact mask design to pattern bridges for J_c measurements. The largest of three bridges was 200 μm by 2 mm and the other two bridges were 100 μm by 0.5 mm and 1 mm, respectively. The patterning laser output was homogenized and focused to a 7 mm by 12 mm spot size to overfill slightly the masked region. During patterning, the laser repetition rate was 10 Hz and an inert gas flow (Ar or N_2) was maintained across the mask to assist in cooling the mask and removing ablated particulates. Twelve 1 mm by 1 mm contact pads were deposited onto the three bridge structures by thermally evaporating silver. A five minute anneal under O_2 at 400 °C improved adhesion and lowered the contact resistance between the silver and the superconductor. The patterned film was wired into a 14 pin IC socket using a low melting indium solder. All I_c measurements were performed at a temperature of boiling liquid N_2 and zero applied magnetic field, using a 1 μV/cm criterion.

3. DISCUSSION AND RESULTS

A. Laser Deposition

The pulsed laser deposition technique was pursued as the physical vapor deposition technique of choice due to its unparalleled research and development versatility. The goals for this work were twofold. First, to develop an understanding of the basic physics and chemistry associated with the laser-target interaction, plume dynamics, and film growth. Second, to develop the technology to produce high-quality HTS ($YBa_2Cu_3O_{7-\delta}$) thin films over larger areas (> 1 sq. in.) which is essential for the development of passive microwave devices. This includes correlating the measured deposition rates and angular distributions, and the parametric dependence of film crystallinity and morphology with laser fluence and spatial profile, repetition rate, wavelengtn, target density and microstructure, ambient pressure and substrate temperature[10].

Parametric Studies. Radial variations in film thickness, fit to $\cos^n(\theta)$, and stoichiometry were investigated[7] as a function of laser fluence, spot size and number of shots (exposure time). Small spot sizes and long exposure times produced broad angular distributions (n=1.5), whereas large spot sizes at short exposure times produced highly forward directed angular distributions (n>8). Under typical spot size (2 mm) and exposure[7], plumes exhibited a $\cos^{3.5}(\theta)$ spread and the resulting films showed a Y deficiency for θ >20°. These results are consistent with a mechanism combining Knudsen layer formation[11],[12], resulting from collisional processes in the high density material within a few microns of the target surface, followed by unstable adiabatic expansion.

Deposition temperature and oxygen pressure were systematically varied between 600-800 °C and 1-20 Pa during film growth. A series of 200 nm

$YBa_2Cu_3O_{7-x}$ films were grown on (100) $Zr(Y)O_2$ substrates (YSZ) as a function of deposition temperatures between 550-800 °C. Dynamic impedance and XRD analysis showed that the best films could be grown at surface temperatures of 750 °C. A systematic variation in the magnitude and transition width of the dynamic impedance response suggests that the growth of epitaxial films is an activated process with an activation barrier of roughly 1.5 eV.

The deposition rate was found to decrease exponentially by up to an order of magnitude then level off at a **PD** product of 54 Pa-cm, where **P** is the static gas pressure and **D** is the target-substrate distance. A similar response has been observed for N_2 and O_2 which suggests that this behavior is not due to reactive scattering, however, Ar and He cause essentially no deposition rate decrease over the same **PD** range. Plume angular distributions and film stoichiometry were found to be independent of oxygen pressures out to 33 Pa, again consistent with Knudsen layer theory [11],[12]. Various post-deposition O_2 anneal protocols were also attempted. The simplest, an increase in the O_2 pressure to 27 kPa for a cool down time of 20 min., was effective to oxygenate the films.

Emission spectra were obtained as a function of pressure from the plume in the spectral region near 600 nm, where both atomic yttrium emission (Y^*) and yttrium monoxide emission (YO^*) could be observed. Figure 2 displays a spectrum obtained at an oxygen pressure of 7×10^{-2} torr. The two starred transitions correspond to Y^* while most of the remaining features are due to YO^*. The ratio of YO^* to Y^* emission was found to change dramatically with pressure of the ambient oxygen atmosphere. In general, it was observed that the ratio YO^*/Y^* increased linearly with pressure at low oxygen pressures, and approached a limiting value at pressures ≥ 0.4 torr.

In order to interpret these results, a kinetic model was developed: reaction of Y with O_2 was assumed to produce all observed YO^*, while the ablation process was assumed to produce Y and Y^*, and collisions were allowed to convert $Y \rightarrow Y^*$, and to quench the various excited states. Applying the steady-state approximation to the model results in the expression: $[YO^*]/[Y^*] = A[O_2]/(B + C[O_2])$, where the constants A,B, and C are sums of products of the rates and rate constants, and $[O_2]$ represents the oxygen pressure. This result obeys the same limiting forms at the experimental data.

These results indicate that collisions play a major role in the laser deposition process. This includes both intra-plume collisions, and plume-gas interactions, which will effect deposition rate and homogeneity. The latter can be seen by simple consideration of gas-kinetic effects. Under typical deposition conditions, the target-substrate distance will be $\approx$ several centimeters, and the pressure of processing gas will be a fraction of a Torr. Gas kinetic theory predicts that this will lead to 1-10 collisions for laser-ablated species between evolution form the target surface and deposition on the substrate. Since $\approx$10 collisions is typically sufficient to relax translationally

excited atoms and small molecules, this means that at the upper end of the range for pressure-distance products that the deposition plume will be diffusing toward the substrate rather than being "sprayed" on as part of a well-directed plume. This places an upper limit on the pressure that can be used for efficient deposition. On the other hand, numerous measurements of chemical speciation in the plume, as well as our recent measurement of chemical reactivity with the processing gas, mandate that a reactive source of oxygen be present in the deposition atmosphere. This, in turn, places a lower limit on the oxygen pressure that can be used for the production of in-situ HTSC films.

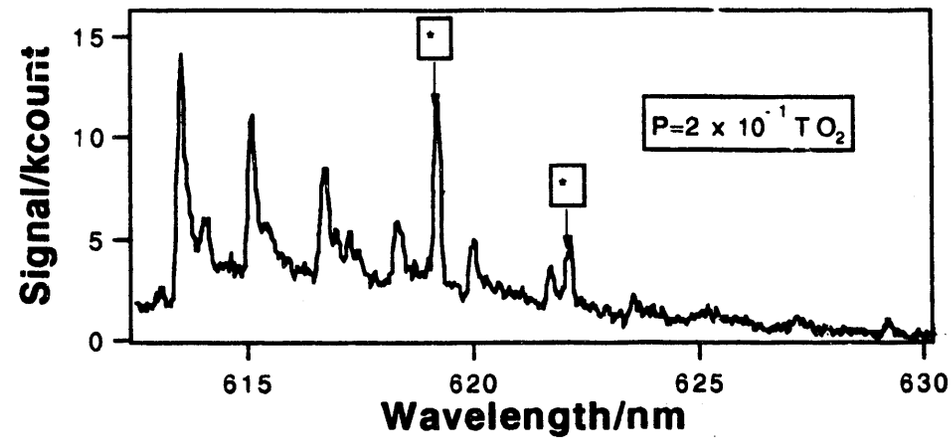

Figure 2. Emission spectrum from ablation of solid Y_2O_3 .

In separate experiments, the quality of superconducting thin films (200 nm thick) of $YBa_2Cu_3O_{7-x}$ on (100) $SrTiO_3$ were monitored as a function of deposition rate from 1 to 14.5 nm/s. The latter exceeded any previously reported deposition rates for epitaxially grown, laser deposited films [13]. Crystallinity of the films was examined by Rutherford backscattering in the channeling mode. The backscattering minimum yield (χ_{min}) was seen to increase monotonically with the deposition (laser repetition) rate. A χ_{min} of 3% was observed in the films deposited at the lowest deposition rate. Even at a deposition rate of 14.5 nm/s, the films show good crystallinity with χ_{min} of 15%, indicating epitaxial growth. Critical current densities $J_c(B=0)$ greater than 10^6 A/cm^2 at 75 K have been measured[5] for films grown on (100) $SrTiO_3$ at deposition rates up to 14.5 nm/sec.

Target modification effects. The deposition rate was always observed to decrease exponentially (by factor 2-10) as a function of laser exposure[14]; when this response is factored out the deposition rate is seen to increase linearly with laser fluence above an evaporation threshold at 0.1-0.5 J/cm^2 out to the highest fluence which we could obtain (30 J/cm^2). As expected, the

deposition rate was found to increase linearly with laser irradiated area for a constant fluence and exposure.

The exposure dependent deposition rate decrease was usually accompanied by the gradual loss of proper stoichiometry (Cu/Y ratio increase) in the deposited films. Electron microprobe analysis of the resulting ablation track (no scanning) on the target showed significant Y enrichment with respect to Ba and Cu[15], as shown in Figure 3.

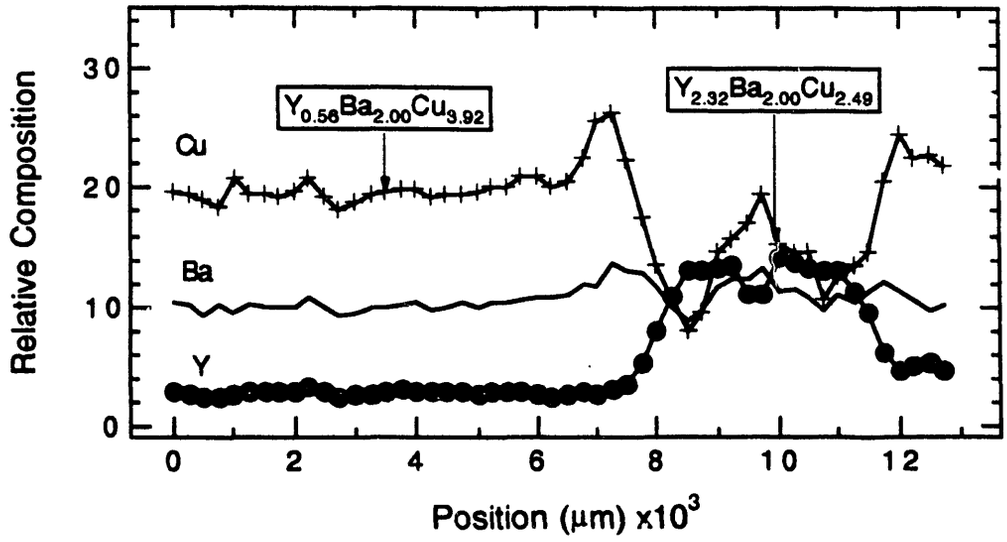

Figure 3. Electron microprobe measurements on exposed(right) and unexposed(left) regions of a YBCO target.

SEM showed adifference in target surface morphology for the laser irradiated (melted) region that in many cases exhibits a columnar regrowth structure. These results suggest that during the ablation process, the incongruently melted zone is larger than the congruently evaporated layer (etch depth). Additionally, microprobe analysis of the target surface unexposed by the laser also showed a relative Y deficiency. This is due to redeposition of Cu and Ba rich particulates from the ablation plume.

B. Laser Writing

We have demonstrated[16] a process for modification of a film's superconducting properties consisting of: 1) deposition of a high-quality HTSC thin film; 2) annealing the film in an Ar-atmosphere which lowers of eliminates T_c; and 3) local re-oxygenation by laser direct-write heating in an O_2 atmosphere. It is important to emphasize that this is a relatively gentle process; the laser heating is used to enhance oxygen diffusion and uptake in the material. The heating is substantially below levels that result in melting or other

structural changes in the $YBa_2Cu_3O_{7-\delta}$ crystal structure[17]. There is no exposure of the HTSC to potential contaminates as is inherent in conventional lithographic and etching fabrication technologies.

The rf-eddy current response for an as-grown $YBa_2Cu_3O_{7-d}$ sample on $LaAlO_3$ showed an onset of the supercurrents in the sample at 92 K. The same type of onset was observed at 58 K after the thermal annealing. Four-point probe measurements confirmed these transitions. Because the annealing procedure was performed under such mild conditions (400° C) the drop in the transition temperature is due to the loss of oxygen in the lattice, rather than alteration of the crystal structure of the material. This allows for relatively easy migration of the oxygen back into the film. Similar responses were observed for the film deposited on $SrTiO_3$.

The rf-eddy current response of the film after the patterning clearly showed two different transitions. A large transition at 58 K was due to the response of the unpatterned material. Because the patterned lines are on the order of 0.4 X 3.0 mm^2, while the total detectable area is approximately 14 mm^2 the percentage of overall material converted to the higher transition temperature was less than 10%. This is consistent with the relatively small transition observed at 92 K. Furthermore, a 4-point measurement of the resistance, which measures only the first percolating pathway and not the amount of superconducting material, clearly showed a resistive transition at 92 K when the probes were on the patterned lines.

C. Laser Modification of Critical Current

In order to produce even simple devices from HTSC films, it may be necessary to control either the transition temperature or critical current with a high degree of precision. In few instances has reproducible modification of film transport properties been demonstrated. It is well established that changing the oxygen content of $YBa_2Cu_3O_{7-\delta}$ can affect the J_c [Singh, 1990 #24]. However, a change in the oxygen stoichiometry also changes T_c of the material[Gupta, 1990 #13].

Previous work involving laser processing of HTSC thin films has concentrated on laser etching [Inam, 1987 #26], patterning [Zheng, 1989 #17], or annealing [Otsubo, 1989 #18]. Recent work by Helvajian has suggested that atom and ion emission can be observed at fluences as low as 50 mJ/cm^2 at 308 nm [Wiedeman, 1990 #14],[Wiedeman, 1991 #15]. The pronounced wavelength dependence of the threshold implies that the mechanism may include a photophysical component. We have examined the electrical and structural behavior of YBCO thin films as a function of 308 nm excimer laser exposure, at fluences below the ablation threshold. This method can lower the J_c of the film with a high degree of accuracy and reliability without significantly lowering T_c.

The superconducting properties of the irradiated films were monitored inductively by dynamic impedance (DI) to determine the effect exposure has on T_c. The dynamic impedance technique uses a single sense/drive coil 6 mm in diameter and placed 0.05 mm above the HTSC sample, and measures the out-of-phase (reactive) component at a set drive frequency. One obtains a direct measure of the impedance change in the coil caused by the coupling between the coil and the eddy-currents induced in the film[Libby, 1971 #23]. Using this monitor, the unirradiated film produced a sharp transition at 91 K with a width of only 1 degree. The inductive transition develops a tail in the curve after laser exposure; however, the onset transition temperature stays at 91 K past 2400 shots. Even after 6000 shots the onset T_c is only reduced by ≈ 4 °C. The inductive transition rapidly deteriorates beyond 6000 shots to 7200 shots; by 7000 shots the film does not show an induction transition.

To further investigate the electrical properties of the laser-irradiated film, I_c measurements were made. The critical current measurements as a function of laser shots and laser fluence are shown in Fig. 4. These measurements indicate that the critical current is a sensitive function of film exposure. At a laser fluence of 20 mJ/cm^2 the film did not indicate any degradation of I_c, while a shot dependent trend does begin at a fluence of 30 mJ/cm^2. This suggests that the modification process has a threshold of 25 ± 5 mJ/cm^2. This modification rate grows rapidly when the fluence is increased to 100 mJ/cm^2. At a constant J_c, I_c is proportional to the thickness of the remaining undamaged layer. The monotonic decrease in I_c can be explained by assuming that the measured critical current is proportional to the thickness of the unmodified layer.

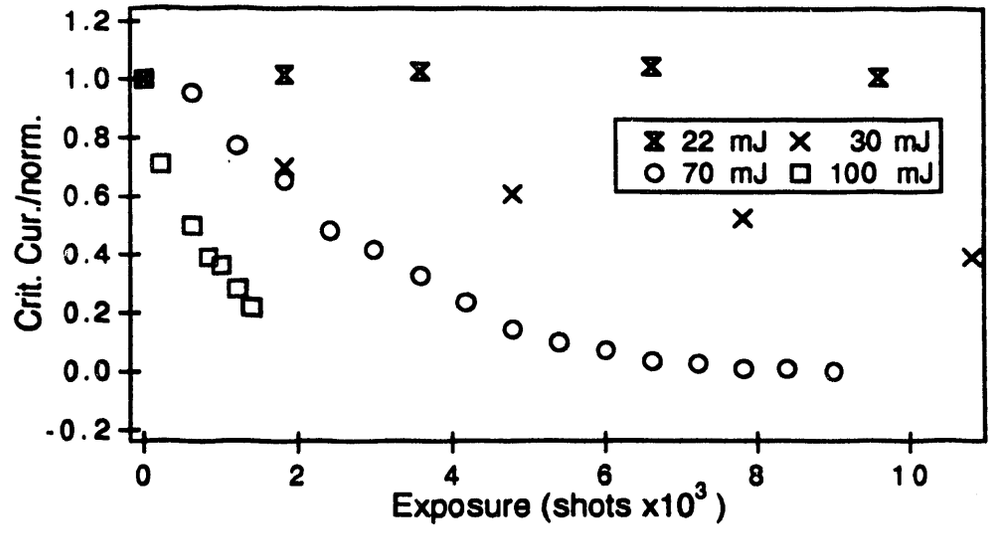

Figure 4. Normalized critical current measurements for laser (308 nm) irradiated films.

Rutherford backscattering (RBS) channeling data also taken on a film exposed to a laser fluence of 70 mJ/cm^2 further indicated that a disordered layer was being formed as a result of laser irradiation. Qualitatively, an increased channeling yield correlates with greater disorder in the film. Furthermore, the shape of the peaks indicated greater disorder at the surface: the surface. Within the error of the RBS measurement no material from the film is being removed, i.e., the film thickness (±10%) and stoichiometry (±3%) remain constant with this laser fluence. At a fluence of 70 mJ/cm^2, SEM showed no visible change in film morphology from that of the unexposed sample. Melting of the film was clearly observed when the fluence is increased to 150 mJ/cm^2. Optical micrographs revealed a slight color change in the film beginning at a fluence of 100 mJ/cm^2.

By adjusting the laser fluence and the number of laser shots the effective J_c in a thin film could thus be controlled to within 255 A/cm^2. The laser damage begins at a fluence of 25 ± 5 mJ/cm^2. Optical changes are observed at a fluence of 100 mJ/cm^2 and melting occurs at 150 mJ/cm^2.

ACKNOWLEDGEMENTS

This work was partially supported by the Superconductivity Pilot Center.

REFERENCES

[1] J. T. Cheung and H. Sankur. Crit. Rev. Solid State Mater. Sci., **15**, 63-109 (1988).

[2] M. Leskela, J. K. Truman, C. H. Mueller and P. H. Holloway. J. Vac. Soc. **A7**, 3147-3171 (1989).

[3] J. Geerk, G. Linker and O. Meyer. Mat. Sci. Reps., **4**, 193-260 (1989).

[4] T. Venkatesan, X.D. Wu, A. Inam, C. C. Chang, M. S. Hegde and B. Dutta. IEEE J. Quantum Electron, **25**, 2388-93 (1989).

[5] X. D. Wu, R. E. Muenchausen, S. Foltyn, R. C. Estler, R. C. Dye, C. Flamme, N. S. Nogar, A. R. Garcia, J. Martin and J. Tesmer. Appl. Phys. Lett., **56**, 1481-3 (1990).

[6] T. VanDuzer. IEEE Jour. of Quant. Electron., 25, 2365 (1989).

[7] R. E. Muenchausen, K. M. Hubbard, S. Foltyn, R. C. Estler, N. S. Nogar and C. Jenkins. Appl. Phys. Lett., **56**, 578-80 (1990).

[8] R. C. Estler, N. S. Nogar, R. E. Muenchausen, X. D. Wu, S. Foltyn and A. R. Garcia. Rev. Sci. Inst., **62**, 437 (1991).

[9] R. C. Dye, N. S. Nogar and R. E. Muenchausen. Chem. Phys. Lett., **181**, 531 (1991).

[10] F. Heidelbach, R. E. Muenchausen, S. R. Foltyn, N. S. Nogar and A .D. Rollett., J. Mater. Res. submitted (1991).

[11] R.W. Kelly and R.W. Dreyfus. Nucl. Instr. and Meth., **B32**, 321-348 (1988).

[12] Roger Kelly. J. Chem. Phys., **92**, 5047-56 (1990).

[13] X. D. Wu, R. E. Muenchausen, S. Foltyn, R. C. Estler, R. C. Dye, A. R. Garcia, N. S. Nogar, P. England, R. Ramesh and a. I. et. Appl. Phys. Lett., **57**, 523-5 (1990).

[14] R. E. Muenchausen, S. R. Foltyn, N. S. Nogar, R. C. Estler, E. J. Peterson and X. D. Wu. Nucl. Instrum. Methods Phys. Res., Sect. A, **A303**, (1991).

[15] S. R. Foltyn, R. C. Dye, K. C. Ott, E. Peterson, K. M. Hubbard, W. Hutchinson, R. E. Muenchausen, R. C. Estler and X. D. Wu. Appl. Phys. Lett., **59**, 594-6 (1991).

[16] R. C. Dye, R. E. Muenchausen, N. S. Nogar, A. Mukherjee and S. R. J. Brueck. Appl. Phys. Lett., **57**, 1149-51 (1990).

[17] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, Jr , W. F. Peck and L. W. Rupp. Physica C, **165**, 419-433 (1990).

DATE
FILMED
12/10/91