Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 439-442

S-I-6

Invited

Advances in the Laser Deposition of High T_c Oxide Superconducting Films at Bellcore/Rutgers

X. D. Wu*, T. Venkatesan, A. Inam*, M. S. Hegde**,
E. W. Chase, B. Dutta*, C. C. Chang, P. England, T. Cheeks,
J. M. Tarascon, J. B. Wachtman**, and W. L. Mclean*

Bellcore, Red Bank, NJ 07701
* Physics Department, Rutgers University, Piscataway, NJ 08854
** Center for Ceramics Research, Rutgers University, Piscataway, NJ 08854

Using pulsed laser deposition technique, high quality Y-Ba-Cu oxide superconducting thin films with critical current densities near 10^6 A/cm^2 at 77 K have been prepared. We have shown that near-single crystal films with state-of-art transport properties can be prepared at a substrate holder temperature of 650 C and below with no post annealing. Stable oxide superconducting thin films directly on silicon have also been fabricated. The results show that the pulsed laser deposition technique is a promising technique for preparing excellent oxide super-conducting thin films, not only for 90 K materials but also for the new higher T_c oxide superconductors.

1. INTRODUCTION

While a number of other techniques have been used to grow high T_c oxide thin films we have used pulsed laser deposition (PLD) technique to prepare these films[1-2]. The advantages of PLD are that it is simple, fast and inexpensive[3]. But the most important benefit of the technique is that films with composition very close to the target stoichiometry can be easily obtained and the composition is independent of the oxygen pressure in the deposition system.

2. EXPERIMENT

A detailed description of the deposition system has been published elsewhere[1,3]. Superconducting or non-superconducting targets of $RE_1Ba_2Cu_3O_x$ were used in the experiments. (100) and (110) $SrTiO_3$, polycrystalline ZrO_2, sapphire and single crystal silicon were the substrates. A Lambda Physik excimer laser (30 ns, 248 nm) was employed. The laser energy density on the target was 1.5 J/cm^2.

3. RESULTS

It was found that there exists an energy density window (1-2 J/cm^2) where high quality films are obtained[4]. For energy density below the lower limit, non-stoichiometric films were obtained. On the other hand, particulates with sizes up to few microns, ejected from the target, were deposited with the films if the energy density was too high. Moreover, films in the central part of the deposited area are stoichiometric while part of the films in the other area are non-stoichiometric[4]. There seems to be evidence for no significant cluster emission, but primary emission of elemental and suboxide species[5]. Particles with super thermal energies are also observed.

The films deposited in vacuum at substrate temperatures up to 500 C were insulating[1,3]. Post-annealing at high temperatures (850-900 C) in oxygen was needed to have zero resistance temperatures over 80 K. The properties of the films were strongly substrate dependent[6], mainly due to the high temperature processing with the best results on $SrTiO_3$ and MgO. Thickness dependence for the films, even on $SrTiO_3$, was also observed [7]. The superconducting films showed preferred orientations: c axis of the films normal to the surface for the films on (100) $SrTiO_3$, c axis in the plane of the films on (110) $SrTiO_3$, and a axis normal to the surface on sapphire. The orientation dependence was observed in both x-ray diffraction[8] and TEM [9] studies. The crystallite sizes (~ 1-2 μm) in the films on $SrTiO_3$ were much larger than those (~ 50 nm) in the films on sapphire because the lattice match between the high T_c superconductor and $SrTiO_3$ is much better. Since the as-deposited films were disordered, the crystallite nucleation can start anywhere in the film during the high temperature annealing. As a result, the annealed films were always polycrystalline in nature. The superconducting properties were affected by the grain boundaries[10-11], at which excess Ba, O, and C were observed using a focussed ion beam induced secondary ion imaging method[12].

As-deposited films, made in a few (~ 5) mTorr oxygen and at substrate temperatures of 650 C, were superconducting at low temperature (~ 30 K). The temperatures quoted were measured on the sample holder since the temperatures measured on the sample surfaces were always lower by 50-150 C and not reproducible. After a low temperature post-annealing at 450 C (compared to 850-900 C) in oxygen, films with zero resistance temperatures as high as 86 K were obtained[13]. The transport properties of 2 μm wide line were similar to those of a 10 μm wide pattern[14] (Fig. 1). X-ray diffaction and TEM studies showed that the films on $SrTiO_3$ were oriented with c axis normal to the surface[15]. A comparison between the films annealed at high temperatures and those made at low temperatures was presented[16]. The results showed that the latter films were superior to the former in surface appearance, interface[17], and transport properties.

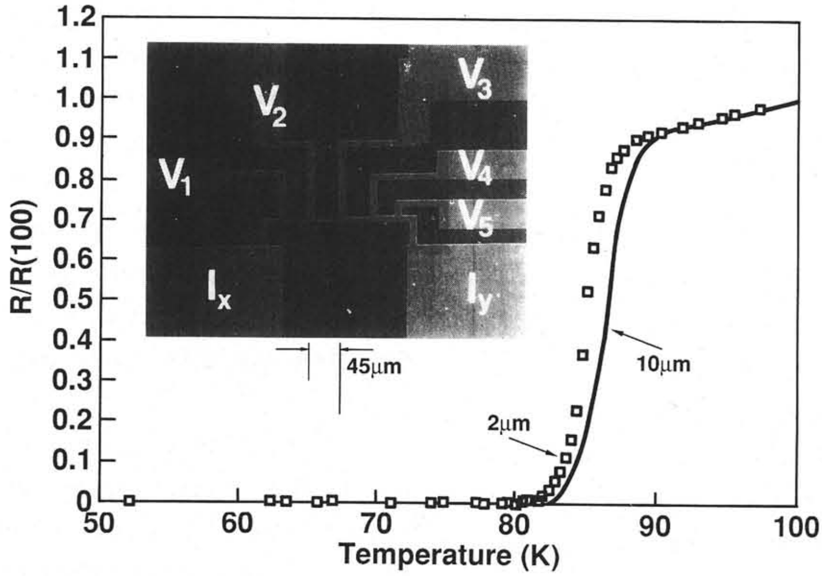

Fig. 1. Superconducting transistions of a 10 μmwide line (solid line) and a 2 μm wide line (symbols). Inset is the geometry used for these comparative measurements. The line widthes in this case are 2, 4, 8, and 10 μm. (ref. 14)

The low temperature processing made it possible to prepare high T_c superconducting thin films directly on silicon [18]. Zero resistance temperatures of 67 K and 80 K were observed on films deposited directly and with a 50 nm ZrO buffer layer on Si respectively. The low temperature, in-situ deposition suppressed the interface reaction between the films and Si.

The laser deposition technique has also been used to prepare Bi-Sr-Ca-Cu oxide films[16]. Films deposited at room temperature in vaccum have compositions very close to those of the targets. After high temperature annealing in oxygen, 80 K superconducting thin films with a small 110 K phase were obtained on $SrTiO_3$. Films with zero resistance about 30 K were prepared using in-situ deposition (600 C). More research is underway.

Moreover, recently we were able to obtain as-deposited Y-Ba-Cu oxide films with zero resistance temperatures about 90 K on $SrTiO_3$ and over 77 K on sapphire at substrate holder temperatures of about 650 C [19] by increasing the overlap of the oxygen fed into the chamber with the laser produced plume. The critical current density measured on a film with a zero resistance temperature of 89 K was $0.7x10^6$ A/cm^2 at 77 K, which is the highest for the films made at such low processing temperatures. These films were found be nearly single crystalline exhibiting an ion channeling minimum yield of 7% (3 Mev He^{++}) as shown in figure 2, implying that over 95% of the atoms are in the right lattice sites[20].

4.CONCLUSION

The pulsed laser deposition technique

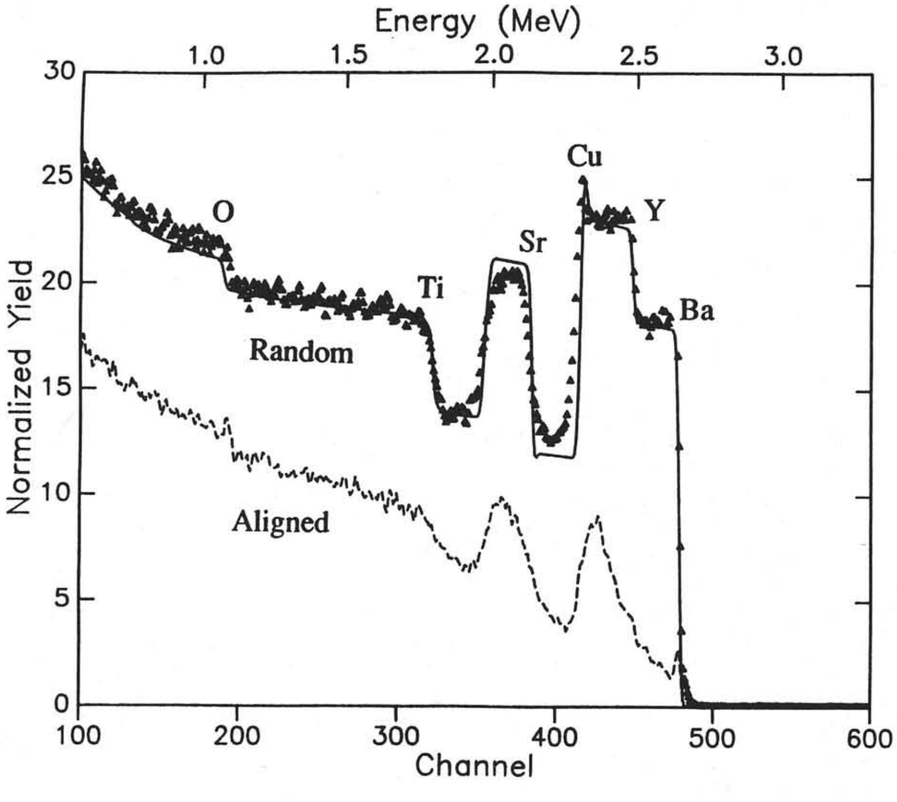

Fig. 2. Random and aligned RBS (3 Mev He^{++}) spectra for an as-deposited Y-Ba-Cu oxide superconducting thin film on (100) $SrTiO_3$. The solid line is a simulation of 4100 Å $Y_1Ba_2Cu_3O_{7-x}/SrTiO_3$. (ref. 20)

is one of best techniques for the preparation of excellent high T_c oxide thin films. The low temperature in-situ processing may enable new possiblities for the applications of the high T_c superconducting thin films.

5.ACKNOWEDGMENTS

The authors would like to thank J. M. Rowell, P. Barboux, L. Nazar, D. M. Hwang, L. H. Greene, B. G. Bagley, P. F. Miceli, R. Krchnavek, M. Croft, and R. Levi-setti for their help.

6. REFERENCES

1) D.Dijkkamp, T.Venkatesan, X.D.Wu, S.A. Shaheen, N.Jisrawi, Y.H.Min-Lee,W.L. McLean, and M.Croft, Appl.Phys.Lett., 51, (1987)619.
2) T.Venkatesan, Solid State Technology, p. 39 (Dec. 1987).
3) X.D.Wu and T.Venkatesan,"Chemistry of Oxide Superconductors, ed. C. N. R. Rao (Blackwell Scientific Publications Ltd., Oxford, UK, 1987).
4) T.Venkatesan, X.D.Wu, A.Inam, and J.B. Wachtman, Appl.Phys.Lett.,52, (1988)1193.
5) T.Venkatesan, X.D.Wu, A.Inam, Y.Jeon, M.Croft, E.W.Chase, C.C.Chang, J.B. Wachtman, R.W.Odom, F.R. di Brozolo, and C.A.Magee, Appl.Phys.Lett.
6) T.Venkatesan, C.C.Chang, D.Dijkkamp, S. B.Ogale, E.W.Chase, L.A.Farrow, D.M. Hwang, P.F.Miceli, S.A.Schwarz, J.M. Tarascon, X.D.Wu, and A.Inam, J.Appl. Phys.,63, (1988)4591.
7) X.D.Wu, D.Dijkkamp, S.B.Ogale, A.Inam, E.W.Chase, P.F.Miceli, C.C.Chang, J.M. Tarascon, and T.Venkatesan, Appl.Phys. Lett., 51, (1987)861.
8) P.F.Miceli, T.Venkatesan, X.D.Wu, and J.A.Potenza, Thin Film Processing and Characterization of High Temperature Superconductors, eds. J.M. E.Harper, R.J.Colton, and L.C.Feldman, (AIP, NY, 1988)p.150.
9) D.M.Hwang, L.Nazar, T.Venkatesan, and X. D.Wu, Appl.Phys.Lett., 52, (1988)1834.
10) S.B.Ogale, D.Dijkkamp, T.Venkatesan,X. D.Wu, and A.Inam, Phys. Rev., B36, (1987)7210.
11) P.England, T.Venkatesan, X.D.Wu, and A. Inam, Phys. Rev. B (unpublished)
12) T.Venkatesan, X.D.Wu, A.Inam, E.W.Chase, C.C.Chang, D.M.Hwang, R.Krchnavek, M.S. Hedge, J.B.Wachtman, W.L.McLean, R. Levi-Setti, J.Chabala, and Y.L.Wang, J. Materials Education, (1988) (in press)
13) X.D.Wu, A.Inam, T.Venkatesan, C.C.Chang, E.W.Chase,P.Barboux, J.M.Tarascon, and B. Wilkens, Appl.Phys.Lett., 52, (1988)754.
14) P. England, (unpublished).
15) D.M.Hwang, (unpublished).
16) X.D.Wu, T.Venkatesan, A.Inam, E.W.Chase, C.C.Chang, Y.Jeon, M.Croft, C.Magee, R. W.Odom, and F.Radicati, High Tc Superconductivity: Thin Films and Devices, (Proc. of SPIE, 1988).
17) C.C.Chang, X.D.Wu, A.Inam, E.W.Chase and T.Venkatesan, Appl.Phys.Lett., (1988) (in press).
18) T.Venkatesan, E.W.Chase, X.D.Wu, A. Inam, C.C.Chang, andF.K.Shokoohi, Appl.Phys. Lett. (1988) (in press).
19) A.Inam, M.S.Hegde, X.D.Wu, T.Venkatesan, E.W.Chase, C.C.Chang, P.England, P.F. Miceli, J.M.Tarascon, and J.B.Wachtman, Appl.Phys.Lett. (1988) (in press).
20) X.D.Wu, A.Inam, M.S.Hedge, T.Venkatesan, E.W.Chase, C.C.Chang, B.Wilkens, and J. M.Tarascon, Phys.Rev. B (unpublished).