NASA Technical Memorandum 103223

Ellipsometric Study of $YBa_2Cu_3O_{7-x}$ Laser Ablated and Co-Evaporated Films

S.A. Alterovitz
Lewis Research Center
Cleveland, Ohio

R.E. Sieg
Cleveland State University
Cleveland, Ohio

J.D. Warner
Lewis Research Center
Cleveland, Ohio

M.A. Stan
Kent State University
Kent, Ohio

S. Vitta
Lewis Research Center
Cleveland, Ohio

Prepared for the
International Conference on Electronic Materials 1990
sponsored by The Materials Research Society
Newark, New Jersey, September 17–19, 1990

NASA

(NASA-TM-103223) ELLIPSOMETRIC STUDY OF YBa2Cu3O(7-x) LASER ABLATED AND CO-EVAPORATED FILMS (NASA) 9 p CSCL 20L

N90-26692

Unclas
G3/76 0297004

ELLIPSOMETRIC STUDY OF $YBa_2Cu_3O_{7-x}$ LASER ABLATED AND CO-EVAPORATED FILMS

S. A. ALTEROVITZ*, R. E. SIEG**, J. D. WARNER*, M. A. STAN+, S. VITTA++
*NASA-Lewis Research Center, Cleveland, Ohio 44135
**Cleveland State University, Dept. of Electrical Engineering, Cleveland, Ohio 44115 and Undergraduate Student Intern at Lewis Research Center
+Kent State University, Department of Physics, Kent, Ohio 44242
++National Research Council - NASA Research Associate at Lewis Research Center

ABSTRACT

High temperature superconducting films of $YBa_2Cu_3O_{7-x}$ (YBCO) were grown on $SrTiO_3$, $LaAlO_3$, and YSZ substrates using two techniques: excimer laser ablation with in-situ annealing and co-evaporation of Y, Cu, and BaF_2 with ex-situ annealing. Film thicknesses were typically 5000 Å, with predominant c-axis alignment perpendicular to the substrate. Critical temperatures up to $T_c(R=0)=90K$ were achieved by both techniques. Ellipsometric measurements were taken in the range 1.6-4.3 eV using a variable angle spectroscopic ellipsometer. The complex dielectric function of the laser ablated films was reproducible from run to run, and was found to be within 10% of that previously reported for (001) oriented single crystals. A dielectric overlayer was observed in these films, with an index of refraction of approximately 1.55 and nearly zero absorption. For the laser ablated films the optical properties were essentially independent of substrate material. The magnitude of the dielectric function obtained for the co-evaporated films was much lower than the value reported for single crystals, and was sample dependent.

INTRODUCTION

Ellipsometry of thin films is a non-destructive technique used to characterize the properties and morphology of thin film materials. It is particularly suitable for thin films since it is non-destructive, highly accurate, and self-normalizing. This last property makes ellipsometry less sensitive to surface irregularities than the conventional optical reflectance technique [1]. Recently several investigators have used ellipsometry to study the dielectric function of sintered pellets [1-4] made from superconducting materials such as YBCO, $CaBi_2Sr_2Cu_2O_8$, and $MBa_2Cu_3O_7$, where M is a lanthanide, as well as single crystal YBCO [1,4]. In general, their results show that the oxygen content has a strong effect on the imaginary part (ϵ_2) of the dielectric function $\epsilon(E)$, but the absolute values depend on the sample. For instance, the measured values of the dielectric function of single crystal samples when compared show very different values in the literature [1,4]. Thus, there is no calibration spectrum that can be used for further ellipsometric studies of morphology and/or overlayers. This fact has essentially prevented any meaningful application of ellipsometry to high temperature superconductors in the last two years.

In this study we will present the application of ellipsometry to the study of sample surface, and overlayer nature and growth rate mainly on laser ablated YBCO superconducting films deposited on several substrates. First, we demonstrate the detection of the presence of a thin overlayer on laser ablated films, its refractive index, thickness, and time evolution. Second, we compare, using SEM and ellipsometry, the surface morphology of YBCO thin films made by two techniques: laser ablation with in-situ oxygen anneal and co-evaporation with ex-situ anneal. Thus, we show that ellipsometry is a valid technique for the evaluation of surface quality in thin HTS films. It is expected that the above study should lead to extensive application of ellipsometry to the investigtion of the surface properties of high temperature superconductors.

EXPERIMENTAL

Samples were prepared by two methods: laser ablation and co-evaporation. The laser ablation technique [5] was based on an excimer laser working at 248 nm, energy density of 1.5 J/cm^2/pulse with 4 pulses per second. The target was a sintered 25 mm diameter YBCO pellet located 8 cm from the sample at 45° to the laser beam. The beam was rastered up and down 1 cm over the target using an external lens on a translator. The substrates used in this study, namely $SrTiO_3$, YSZ (yttria stabilized ZrO_2), and $LaAlO_3$, were mounted on a stainless steel plate with a diameter of 63 mm. The plate was heated from the backside by resistive heating, while a type K thermocouple, welded to the plate, was used for thermometry. After a preheat to 600 °C, oxygen was introduced into the chamber and the samples were heated to temperatures at or near 775 °C. During deposition an oxygen pressure of 170 mTorr was maintained using a 15 sccm flow of oxygen. After deposition the oxygen pressure was raised to 1 atm and the temperature was lowered slowly (at a rate of 2 °C/min) to 450 °C, maintained there for 2 hours, then lowered slowly to 250 °C and finally cooled below 40 °C for removal. The co-evaporation method was essentially the same as the one described in reference [6]. Two electron guns were used to evaporate Y and Cu while thermal evaporation was used for BaF_2. The ex-situ anneal step started with wet oxygen for 1 hour at 875 °C, followed by a dry oxygen anneal, 1 hour step down to 550 °C, 1 hour at 550 °C, and finally oven cool down. The critical temperature, T_c, was measured resistively using a four point technique. In some cases the actual samples were tested, while other times samples made in the same run were measured. The ellipsometric technique was described elsewhere [7] and will not be repeated here. Analysis of the results was done mainly using a substrate and ambient model, while in some cases a substrate, film, and ambient model was applied. Rough surfaces were modeled by a combination of voids and substrate material using the effective medium approximation (EMA) [8].

RESULTS

Results reported here were obtained on samples prepared in separate runs on both the laser ablation and co-evaporation techniques. All samples show c-axis alignment, with only (001) peaks present in the X-ray diffraction pattern. Altogether 12 laser ablated and 5 co-evaporated films were measured. Data will be reported only for samples with a $T_c(R=0)$ higher than 82 K. This is essentially all of the films since a $T_c(R=0)$ higher than 85 K was characteristic of most of the films, especially in the case of the laser ablated films. The thickness of the films was typically 5000 Å, thus ensuring that it was much larger than the optical penetration depth. Several measurements at different angles of incidence, in the range 65°-75°, were performed for all samples. The measured ellipsometric parameters $\tan(\psi)$ and $\cos(\Delta)$ were used to calculate the dielectric function, ϵ, directly.The results gave essentially the same value of the dielectric function, ϵ, independent of the angle of incidence for the samples shown here. Results for ϵ for four representative samples made by laser ablation are compared with that of single crystal YBCO [4] in Fig. 1.

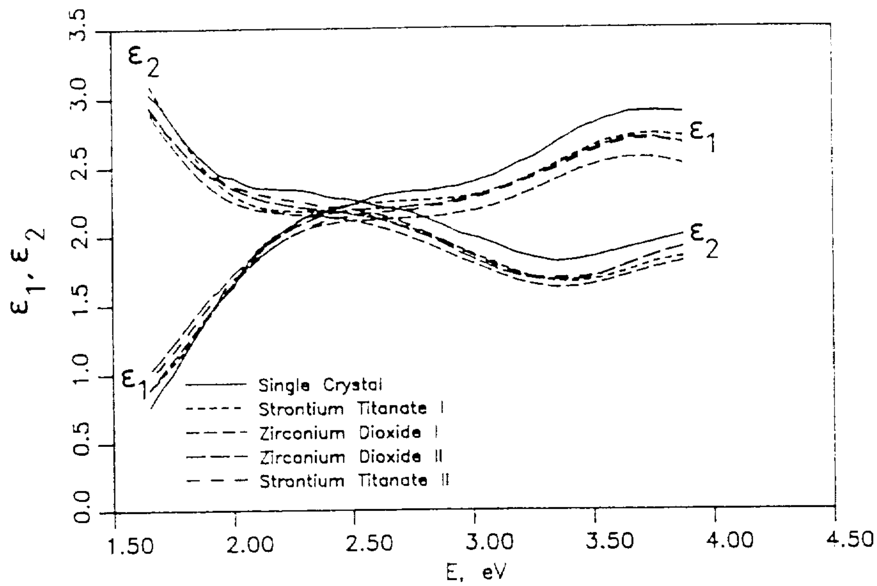

FIGURE 1. - DIELECTRIC FUNCTION OF FOUR LASER ABLATED FILMS AND A SINGLE CRYSTAL YBCO [4].

All laser ablated samples, irrespective of the substrate material, gave dielectric functions with very similar shapes. However, some of them gave absolute values lower than the majority. The lowest $\epsilon(E)$ values obtained for any laser ablated sample are shown in Fig. 2, labeled "before Q tip cleaning".

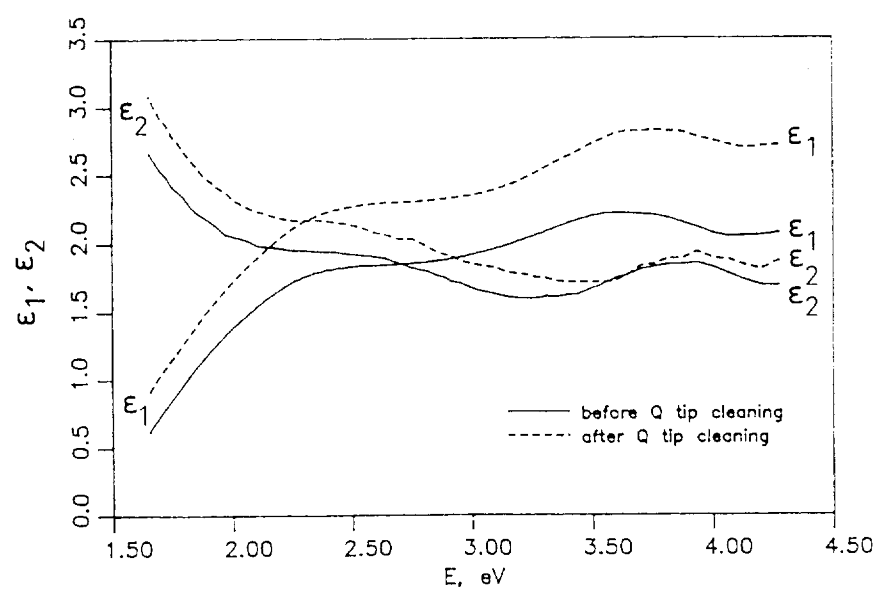

FIGURE 2. - DIELECTRIC FUNCTION OF A LASER ABLATED FILM BEFORE AND AFTER MECHANICAL CLEANING.

In the course of making electrical contacts to the laser ablated films, we found that the quality of the contacts is poor. A solution to this problem was mechanical cleaning of the surface. This fact is related to the result previously reported for YBCO, namely the interaction with air to produce $BaCO_3$ and $Ba(OH)_2$ [9-11]. Mechanical cleaning with a Q tip removed a small amount of material from the surface of these films with low values of the dielectric function. Fig. 2 displays ϵ before and after mechanical cleaning. Cleaning was done with the sample in the ellipsometer, with dry nitrogen flow kept for the measurement. The difference between these two spectra was analyzed as follows: $\epsilon(E)$ after mechanical cleaning was assumed as the calibration $\epsilon(E)$, while the result for $\epsilon(E)$ before cleaning was analyzed as substrate-dielectric film-ambient. The refractive index of the 72 Å film was found to be 1.55. Moreover, it is not a function of energy, as is required for an insulator. This value of the refractive index is in good agreement with published data [12] for $BaCO_3$, but not for $Ba(OH)_2$. The $BaCO_3$ film growth rate in air, at temperatures around 20 °C, was studied by measuring the film thickness versus time. Measurements started immediately after the mechanical cleaning and lasted 480 hours. The final thickness was 35 Å, showing a rather slow growth rate, of the order of 1.5 Å/day, for this sample. We found that the quality of electrical contacts made by silver evaporation and annealing in oxygen depends on the thickness of the dielectric layer. In the worst cases, the silver contact would peel off the sample when a small force was applied. Results of $\epsilon(E)$ functions of cleaned samples show much less variation in absolute value versus the original measurements.

Dielectric functions of two co-evaporated samples are shown in Fig. 3. $\epsilon(E)$ in this case is sample dependent and bear small similarity to the single crystal result. SEM micrographs of the films show the presence of voids on otherwise dense films. In addition, the films show more roughness on the surface as compared to the laser ablated films which have <0.25 μm surface roughness as seen by SEM.

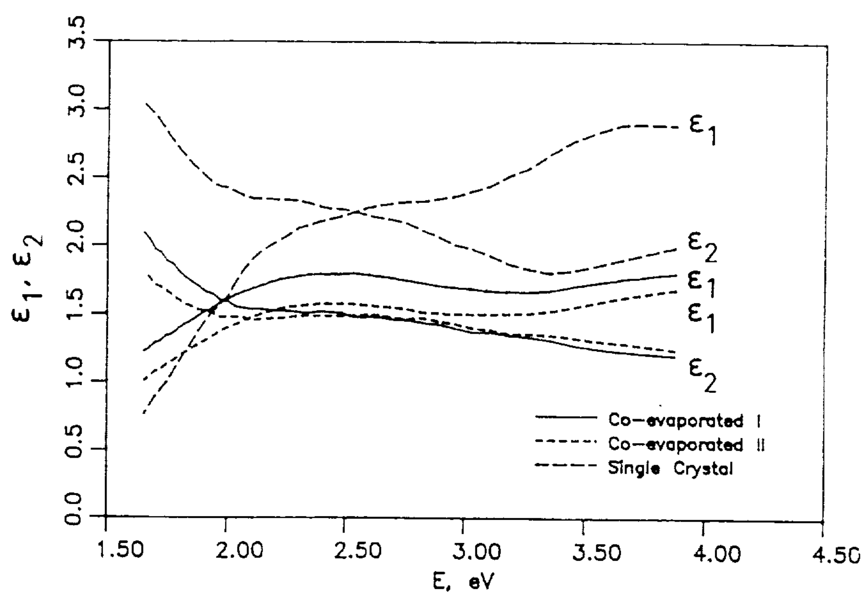

FIGURE 3. - DIELECTRIC FUNCTION OF TWO COEVAPORATED FILMS AND A SINGLE CRYSTAL YBCO [4].

We tried to describe the morphology by the EMA method [8], i.e. using a combination of voids and YBCO. The free parameter used was the void volume fraction, f. A test of the quality of this model is given in Fig. 4, where the best value of f (25.8%) was used to generate ψ and Δ, and compared with the experimental results. The quality of the fit is only moderate, showing that this model is marginally applicable. We obtained large void fractions typically around 20-25%.

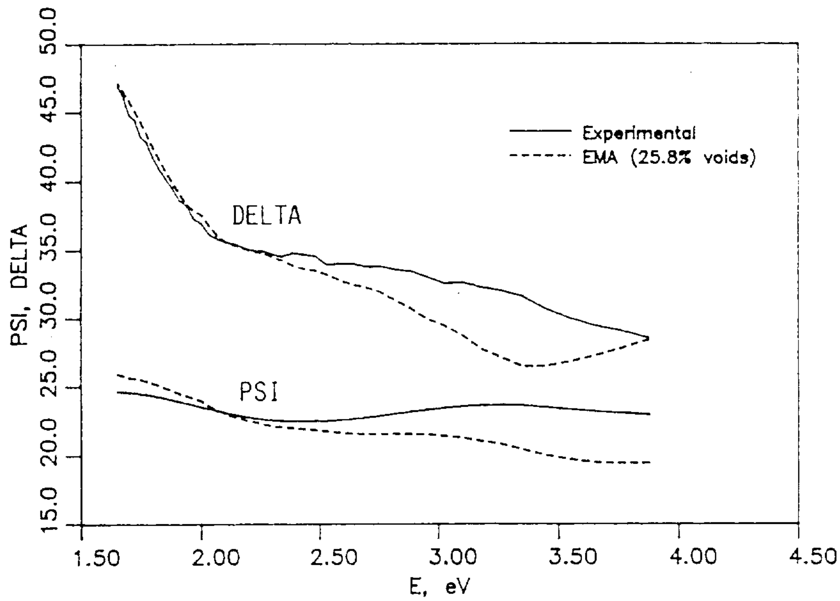

FIGURE 4. - CALCULATED AND EXPERIMENTAL PSI AND DELTA VERSUS ENERGY FOR A COEVAPORATED YBCO FILM.

DISCUSSION

Evaluation of a dielectric function for ellipsometric characterization purposes requires an absolutely perfect surface. As YBCO reacts with air, and the surface morphology of this new type of material is not completely under control, the $\epsilon(E)$ determination is not a simple matter. Our results show a scatter just below 10% among themselves and versus the single crystal result. The best analysis of the overlayers, which are below 10 Å in many cases, is reached when the $\epsilon(E)$ of the cleaned sample is used as the substrate $\epsilon(E)$, i.e. not by using a universal $\epsilon(E)$ function. In this way surface irregularities do not interfere with the overlayer analysis. The fact that our results are so similar to the single crystal result of reference [4] shows that the laser ablation technique gives smooth crystalline films and that the $\epsilon(E)$ given in [4] is for a good quality single crystal. The overlayer, probably $BaCO_3$, was shown to grow very slowly. However, we believe that the growth rate depends on the stoichiometry of the material on the top surface layer. Thus, the experimental growth rate measured here is only for one particular case, obtained for a high quality crystalline film.

The EMA analysis of the co-evaporated films was not completely successful. The reasons for this, in our opinion, are mainly the complex nature of the surface roughness, and, to a lesser extent, the imperfect stoichiometry on the surface of these films. We expect the void fraction to be a function of depth, with lower values of f as we move into the film. These facts, along with the

CONCLUSIONS

We obtained reproducible results for the dielectric function on fully c-axis aligned samples. In absolute value, this result is very similar to the function obtained for (001), platelet-like, free-grown, single crystals [4]. The differences are smaller than 10% at any value of the spectrum. We used our result as the calibration spectrum for subsequent studies, although the single crystal result of reference [4] is probably just as reliable. An overlayer of $BaCO_3$ was measured on top of these films and its growth rate was determined. Results of the overlayer properties analysis compare favorably with the literature. The comparison of the ellipsometry and SEM studies shows that smoothness and density of the film surface are the crucial parameters in the ellipsometric results on YBCO films.

ACKNOWLEDGEMENT

We are indebted to John H. Scofield for allowing us to use his co-evaporation system.

REFERENCES

[1] M. Garriga, J. Humlicek, J. Barth, R. L. Johnson, and M. Cardona, J. Opt. Soc. Am. **B6**, 470 (1989).
[2] M. K. Kelly, Siu-Wai Chan, K. Jenkin II, D. E. Aspnes, P. Barboux, and J. M. Tarascon, Appl. Phys. Lett. **53**, 2333 (1988).
[3] M. K. Kelly, D. E. Aspnes, P. Barboux, J. M. Tarascon, Siu-Wai Chan, and K. Jenkin II, SPIE Conf. Proc. **1056**, 212 (1989).
[4] M. K. Kelly, P. Barboux, J. M. Tarascon, D. E. Aspnes, W. A. Bonner, and P. A. Morris, Phys. Rev. B **38**, 870 (1988).
[5] J. D. Warner, J. E. Meola, and K. A. Jenkins, NASA TM-102350 (1989).
[6] P. M. Mankiewich, J. H. Scofield, W. J. Skocpol, R. E. Howard, A. H. Dayem, and E. Good, Appl. Phys. Lett. **51**, 1753 (1987).
[7] S. A. Alterovitz, R. M. Sieg, N. S. Shoemaker, and J. J. Pouch, Mat. Res. Soc. Symp. Proc. **152**, 21 (1989).
[8] D. E. Aspnes, J. B. Theeten, and F. Hottier, Phys. Rev. B **20**, 3292 (1979).
[9] M. F. Fan, R. L. Barns, H. M. O'Brian Jr., P. K. Gallagher, R. C. Sherwood, and S. Jin, Appl. Phys. Lett. **51**, 532 (1987).
[10] Narottam P. Bansal and Ann L. Sandkuhl, Appl. Phys. Lett. **52**, 323 (1988).
[11] R. P. Vasquez, B. D. Hunt, and M. C. Foote, Appl. Phys. Lett. **53**, 2692 (1988).
[12] CRC Handbook of Chemistry and Physics, 65th Edition, Robert C. Weast ed., CRC Press, Boca Raton, Florida (1984).

NASA
National Aeronautics and Space Administration

Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-103223		

4. Title and Subtitle
Ellipsometric Study of $YBa_2Cu_3O_{7-x}$ Laser Ablated and Co-Evaporated Films

5. Report Date

6. Performing Organization Code

7. Author(s)
S.A. Alterovitz, R.E. Sieg, J.D. Warner, M.A. Stan, and S. Vitta

8. Performing Organization Report No.
E-5637

10. Work Unit No.
505-44-2C

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

11. Contract or Grant No.

13. Type of Report and Period Covered
Technical Memorandum

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546-0001

14. Sponsoring Agency Code

15. Supplementary Notes

Prepared for the International Conference on Electronic Materials 1990 sponsored by The Materials Research Society, Newark, New Jersey, September 17-19, 1990. S.A. Alterovitz and J.D. Warner, NASA Lewis Research Center. R.E. Sieg, Cleveland State University, Dept. of Electrical Engineering, Cleveland, Ohio 44115 and Undergraduate Student Intern at Lewis Research Center. M.A. Stan, Kent State University, Dept. of Physics, Kent, Ohio 44242. S. Vitta, National Research Council—NASA Research Associate at Lewis Research Center.

16. Abstract

High temperature superconducting films of $YBa_2Cu_3O_{7-x}$ (YBCO) were grown on $SrTiO_3$, $LaAlO_3$, and YSZ substrates using two techniques: excimer laser ablation with in-situ annealing and co-evaporation of Y, Cu, and BaF_2 with ex-situ annealing. Film thicknesses were typically 5000 Å, with predominant c-axis alignment perpendicular to the substrate. Critical temperatures up to $Tc(R = 0) = 90K$ were achieved by both techniques. Ellipsometric measurements were taken in the range 1.6-4.3 eV using a variable angle spectroscopic ellipsometer. The complex dielectric function of the laser ablated films was reproducible from run to run, and was found to be within 10% of that previously reported for (001) oriented single crystals. A dielectric overlayer was observed in these films, with an index of refraction of approximately 1.55 and nearly zero absorption. For the laser ablated films the optical properties were essentially independent of substrate material. The magnitude of the dielectric function obtained for the co-evaported films was much lower than the value reported for single crystals, and was sample dependent.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
High temperature superconductors Ellipsometry	Unclassified – Unlimited Subject Category 76

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified	7	A02

NASA FORM 1626 OCT 86

*For sale by the National Technical Information Service, Springfield, Virginia 22161