

Spectroscopic ellipsometry studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposited on SrTiO_3

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The dielectric function $\epsilon = \epsilon_1 - i\epsilon_2$ of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high- T_c superconducting films grown on (100) SrTiO_3 (c -axis oriented) and (110) SrTiO_3 (ab -oriented) substrate was measured by spectroscopic polarization modulation ellipsometry (SPME) and changes in film orientation were studied by comparing films of various thicknesses. The films deposited on SrTiO_3 (100) substrates demonstrated an isotropic ϵ_1 that changed with film thickness. It is observed that the decrease in the metallic dielectric behavior associated with the increase in the thickness of the films grown on (100) SrTiO_3 substrates is mainly due to a change in the orientation of the films. The films deposited on SrTiO_3 (110) showed anisotropic dielectric behavior when the plane of polarization is parallel and perpendicular to the c -axis of the film. These studies show that for this high-temperature superconductor with anisotropic dielectric behavior, SPME is a highly sensitive technique capable of measuring small changes in the film orientation.

I. INTRODUCTION

The potential uses of the high-temperature superconductor Y-Ba-Cu-O in electronic applications will rely heavily on the ability to make and process thin films of these materials and control optical and hence transport properties of the material. An obvious extension of the knowledge required to control these properties is an understanding of the effect of film thickness on the optical constants of thin films of this copper-oxide superconductor. Although thin films and superlattices with high transition critical temperatures have been grown by various techniques,¹⁻⁴ the structures are still far from those of ideal single crystals. Until now, the best $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films have been grown only on SrTiO_3 substrates.¹ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is highly anisotropic⁵ and the electronic excitation in the a - b plane shows a metallic characteristic while the electronic characteristic in the c -direction shows a more insulatorlike behavior. Therefore, a good control of the film orientation is extremely important in crystal growth. In general, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown on (100) SrTiO_3 substrate result in c -oriented films (a, b axes in the plane of the film), while films grown on (110) SrTiO_3 substrate are ab -oriented (c -axis in the plane of the film). However, with an increase in the film thickness these general rules for film orientation based on the orientation of their substrates may not be applicable. For relatively thick films, a mixture of a -, b - and c -axes may incorporate into the film plane creating random orientation.

Film orientation and other related properties may be examined by many characterization techniques.⁶⁻²¹ Among them, reflectance measurements have been used extensively.⁸⁻²¹ However, thus far, there has been no systematic study which has established the change in the optical constants of this material as a function of the film thickness. In this study, we investigate the optical response

of the Y-Ba-Cu-O films grown on SrTiO_3 substrates using spectroscopic polarization modulation ellipsometry (SPME).^{22,23} In particular, measurements of the dielectric function in this anisotropic material can be related to the film orientation. We will compare the films grown on both (100) and (110) SrTiO_3 substrates with various thicknesses and explicitly show that the orientation changes with film thickness. Our results also demonstrate that SPME can be used as a powerful characterization technique for investigating the orientations of the high temperature superconducting films.

II. EXPERIMENT

The Y-Ba-Cu-O samples studied here were grown on substrates of SrTiO_3 (100) and SrTiO_3 (110). The samples examined were $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films deposited on SrTiO_3 (100) substrates with thicknesses of 50, 110, 200, and 1200 nm, and deposited on SrTiO_3 (110) substrates with thicknesses of 110 and 250 nm. Laser depositions were performed by ablating a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ target by a Q -switched Nd:YAG laser (Spectra Physics DCR-3) in a vacuum chamber with base pressure $\sim 1 \times 10^{-4}$ Torr. The laser beam was focused, through an optical window, to a 1-mm diameter spot on the target at an angle of 15° relative to the target surface. The substrates were mounted parallel to the target at a distance of 4 cm on a small heater. The laser was operated at a wavelength of 1064 nm with a pulse energy of 100–200 mJ and a repetition rate of 30 Hz. Substrate temperature was nominally maintained at 750°C and the oxygen pressure during ablation was 200 mTorr. Films were slowly cooled in oxygen ambient and thus post-annealing was not necessary. The smoothness of the films was improved dramatically by introducing a quartz rod between the target and the substrates so that the direct plume from the target is completely blocked from the substrate. Subse-

quently the specimens were examined by x-ray powder diffraction to insure the proper stoichiometry and crystalline orientation. The approximate value of thicknesses were obtained using profilometry.

We have used the SPME technique similar to the one used by Bermudez and Ritz to measure the dielectric response of the specimens.^{22,23} The dielectric function for the substrate was measured first and then the dielectric function for the entire sample was measured (substrate and film). Hence, the dielectric function for the film itself can be derived from the measured data using the two-phase model.²⁴ All measurements were taken at room temperature.

One of the error sources for the dielectric functions for the films is the uncertainty of the film thickness. Using a 10% variation in the thickness of the 50 nm film, we have determined that the uncertainty of the dielectric function derived from the measured data is less than 10%. The estimated uncertainty in the dielectric functions decreases as the film thickness increases.

III. RESULTS AND DISCUSSION

The real and the imaginary parts of the dielectric function ϵ_1 and ϵ_2 for films grown on (100) SrTiO₃ substrates with various thicknesses are shown in Fig. 1. The spectra are taken from 1.5 to 3 eV. For the films with thicknesses below 200 nm, the imaginary part of the dielectric function ϵ_2 increases with decreasing energy, while the real part of the dielectric function ϵ_1 decreases with decreasing energy. Below a particular energy (called the critical energy E_c), the real part of the dielectric function ϵ_1 becomes negative. The resultant dielectric function shows a general metallic behavior and the critical energy E_c then can be approximately related to the plasma energy E_p of the material^{11,25}

$$E_p^2 = \left(E_c^2 + \frac{\hbar^2}{r^2} \right) \epsilon_\infty.$$

By examining the results shown in Fig. 1, we find that the dielectric function measured from the samples with different thicknesses shows a general trend. In other words, the optical response exhibits a dependence on the film thickness. Specifically, the critical energy position E_c decreases consistently with an increase in the film thickness. For the film with a thickness of 50 nm, the critical energy is 2.8 eV. When the film thickness increases to 200 nm, the critical energy reduces to about 1.5 eV. The decrease in the critical energy implies a decrease in the plasma energy and indicates that the material loses its metallic dielectric behavior as the film thickness is increased.

The dielectric function of the films measured with SPME is the average response of many small single crystals or microcrystals which form the region of the film being probed by the incident beam. Therefore, the plasma energy derived from the critical energy also represents an average value. For a perfectly *c*-oriented film the microcrystals forming the film all have *c*-axis orientation with *a* and *b* in the plane of the film. Hence the dielectric function will show a metallic behavior. However, for a perfectly *ab*-

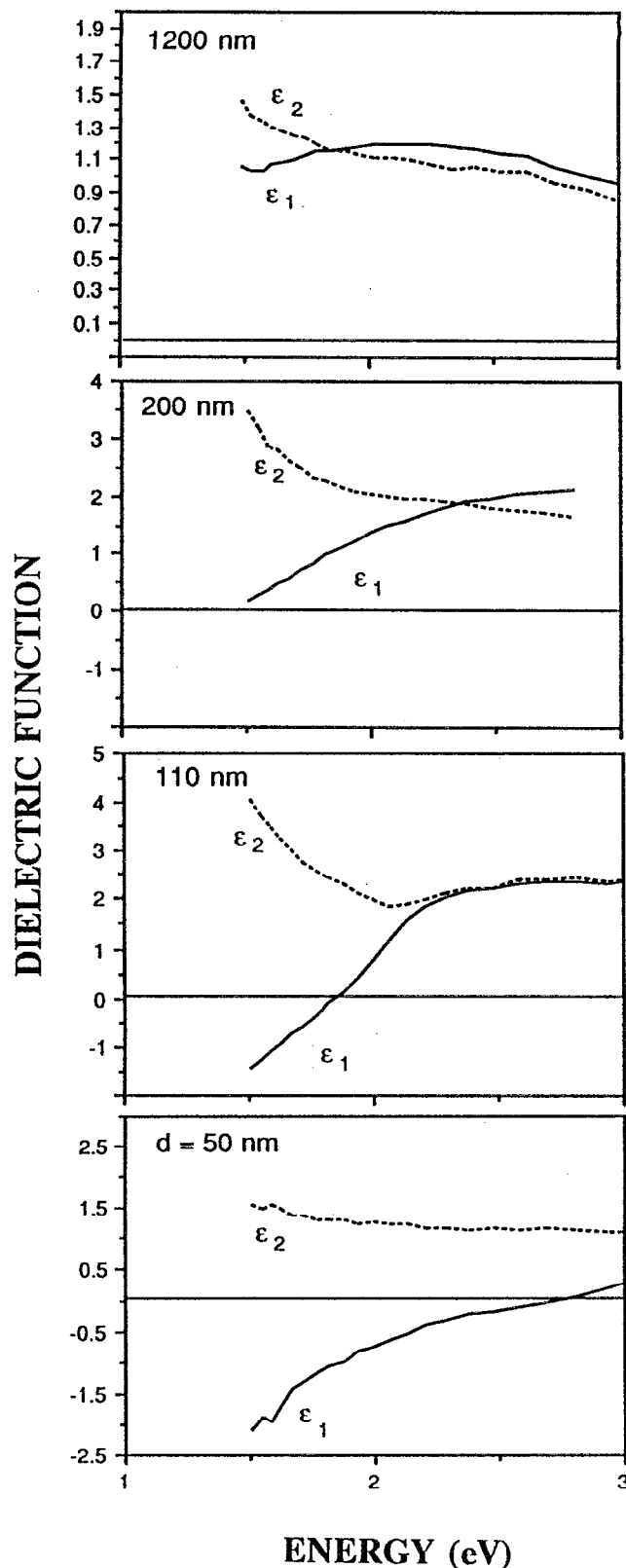


FIG. 1. Dielectric function $\epsilon_1 - i\epsilon_2$ for various thicknesses of YBa₂Cu₃O_{7- δ} films deposited on SrTiO₃ (100).

oriented film, the *c*-axis of all the microcrystals will lie in the plane of the film. In the latter case depending on whether the probe beam is polarized perpendicular or par-

allel to the c -axis, a metallike or insulatorlike response will be observed.

From the above discussion, it is clear that a decrease in the critical or plasma energy represents a change in the crystal orientation. For thin films, where the microcrystals in the film are mainly oriented in the c -direction perpendicular to the film plane, higher plasma energies and corresponding metallic dielectric behavior are observed. When the film thickness increases, the films are no longer perfectly c -axis oriented and the c -axis is partially incorporated into the film plane. Thus, the films lose their metallic dielectric behavior due to the partial contribution from excitations along the c -axis. The increase in the degree of random orientation was also observed by comparing our measured optical constants obtained for the 1200-nm thick film (which are shown in Fig. 1) to those of a bulk ceramic sample (which is in general randomly oriented). In both cases, the real part of the dielectric function does not become negative in the energy region that we have examined (down to 1.5 eV).

The dielectric functions for the films grown on (110) SrTiO₃ substrates are shown in Fig. 2 as a function of the direction of the polarization of the incident beam with respect to the c -axis of the films. The thicknesses for the two films are 110 and 250 nm. The spectra were taken from 1.5 to 3 eV. The ϵ spectra were obtained for $\theta = n(\pi/4)$ rotations of the sample where $n = 0, 1, 2, 3, 4$, and θ = the angle between the c -axis of the crystal and the plane of polarization. The spectra shown in Fig. 2 correspond to rotations of $n = 0, 1$ and 2.

Unlike the films grown on (100) substrates, the results strongly depend on the direction of the optical polarization in the plane. When the polarization is perpendicular to the c -axis the measured dielectric function shows a metallic behavior that is similar to films grown on (100) SrTiO₃ with similar thicknesses. When the sample is rotated by 45° and 90°, the observed response more closely resembles insulatorlike dielectric behavior. The above-described data show a gradual change of the dielectric response with orientation. These observations are attributed to the conductance anisotropy between the c -axis and ab -axes which are contained within the film plane.

As seen in Fig. 2 the critical energy position observed for the 250-nm thick film changes only slightly as compared to the 110-nm thick film. However, for the films grown on (100) substrate the critical energy changes by much greater amounts as the film thickness increases as shown in Fig. 1. As we have already discussed, when the films are grown on (100) SrTiO₃ the c -axis becomes incorporated into the plane of the film as the thickness is increased. For films grown on (110) substrate since the c -axis is initially in the film plane as the thickness is increased the c -axis may come out of the plane. The change in ϵ with film thickness for films on (110) substrate, however, is much less than that observed for the films on (100) SrTiO₃. Therefore, this indicates that it is more likely for the c -axis to become incorporated into the plane of the films on (100) SrTiO₃ than it is for the c -axis to come out of the plane of the films on (110) SrTiO₃. In other words,

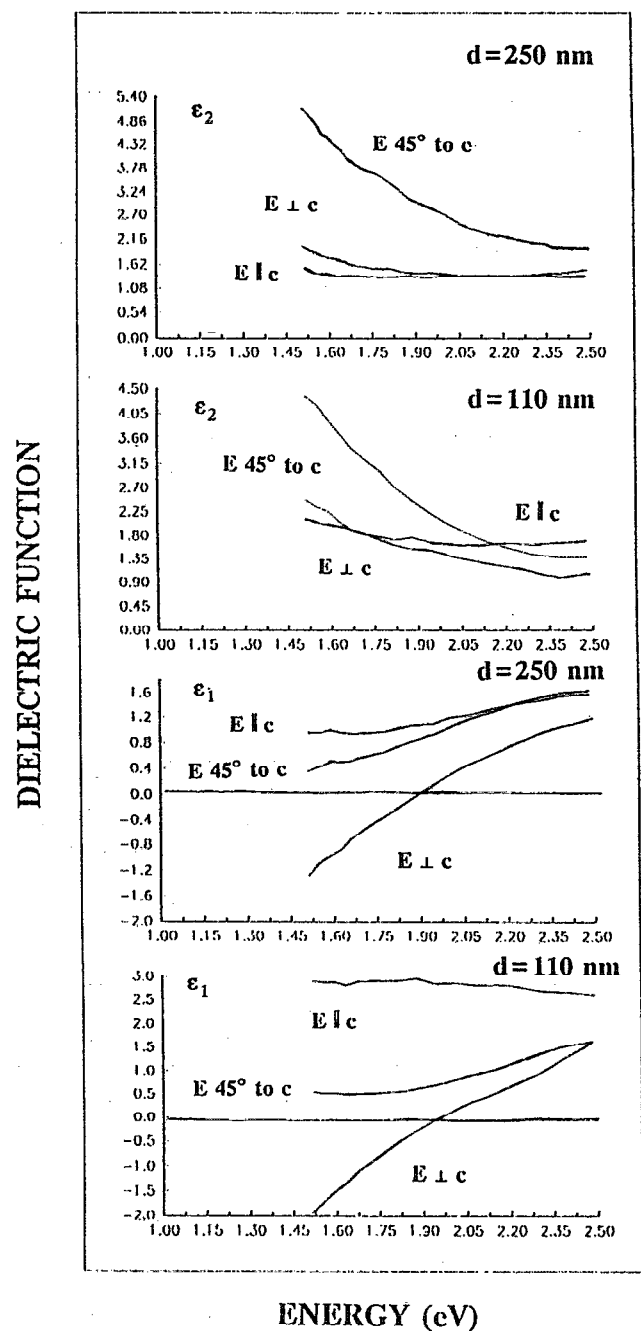


FIG. 2. Dielectric function $\epsilon_1 - i\epsilon_2$ for a 110- and 250-nm-thick YBa₂Cu₃O_{7- δ} film deposited on SrTiO₃ (110), with axis of polarization parallel, at 45°, and perpendicular to the c -axis.

the orientation changes more significantly with film thickness for our films grown on (100) SrTiO₃ than it does for our films grown on (110) SrTiO₃. This observation is very useful in applications.

To further demonstrate that the films grown on (100) SrTiO₃ substrate result in mainly c -axis orientation when the thickness is sufficiently small, we compared the two samples with thicknesses of 110 nm grown on the (100) and (110) substrates. The results are shown in Fig. 3 with the optical polarization of the probe beam perpendicular to the c -axis of the (110) ab -oriented film. The similarity of

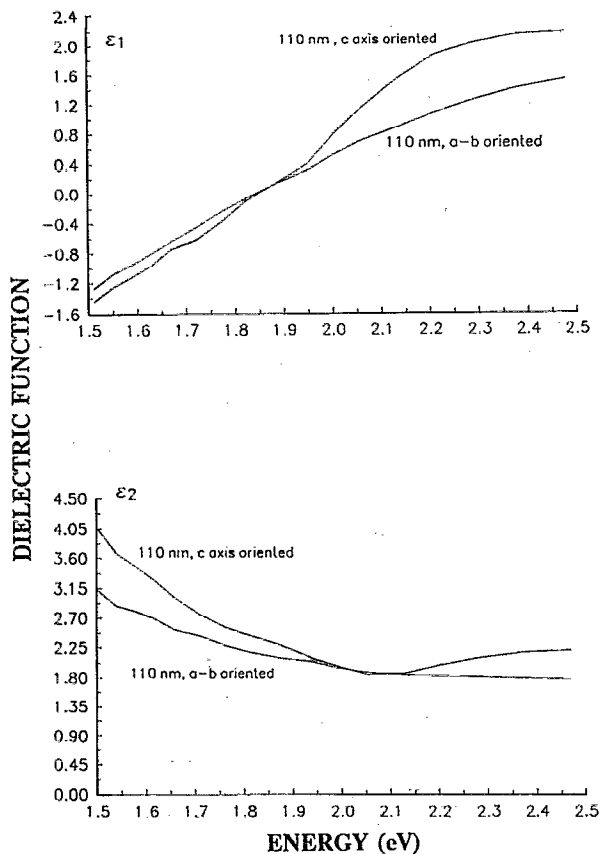


FIG. 3. Comparison of ϵ_1 and ϵ_2 for the 110-nm-thick *c*-axis oriented and *ab*-oriented (with polarization perpendicular to the *c*-axis) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films.

the dielectric functions for these two samples are expected, since in both cases the optical polarization is in the *ab* plane. Consequently, the observed optical response for both films show metallic dielectric behavior as would be expected for the CuO_2 (*ab*) plane.

Finally, we compared the results from the 1200-nm thick film grown on (100) SrTiO_3 substrate with the 110-nm thick thin film grown on the (110) SrTiO_3 substrate. The spectra are shown in Fig. 4 with the polarization along the *c*-axis for the latter film. Although the magnitude of the dielectric functions are somewhat different, the line shapes are very similar. Both of them are relatively flat and no metallic dielectric behavior is observed as both do not exhibit any critical energy positions. Therefore, this independently demonstrates that the *c*-axis actually becomes incorporated into the film plane when the thicknesses of the films grown on (100) substrate are increased.

The magnitude of the fluctuation in the dielectric function observed in the above comparison may be primarily due to surface roughness and possibly due to surface oxide or contaminant layers associated with the various samples. Due to this reason, we have not attempted to analyze our optical spectra quantitatively at this time. The main point we want to make is that the results obtained from the ellipsometry measurements can be directly related to the orientation of the high- T_c films grown on various sub-

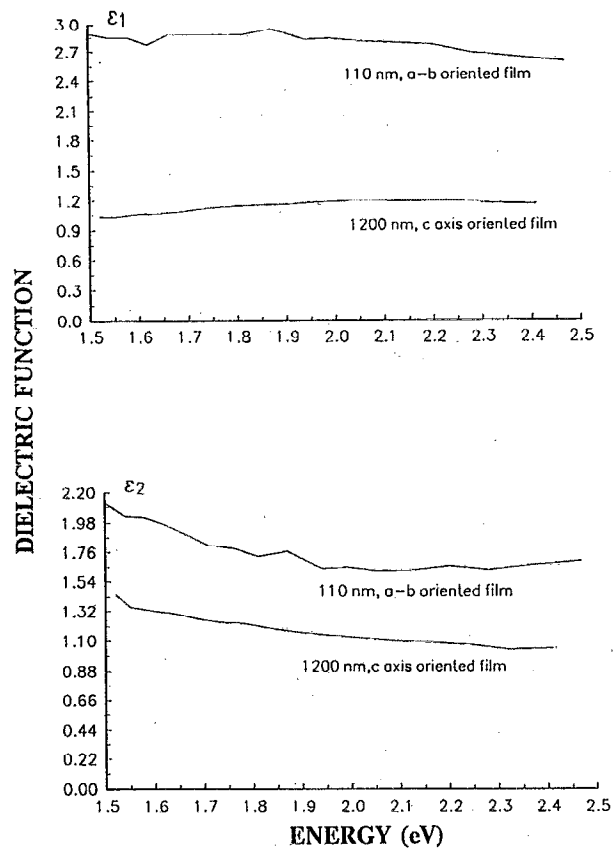


FIG. 4. Comparison of ϵ_1 and ϵ_2 for the 1200-nm-thick *c*-axis oriented and 110-nm thick *ab*-oriented (with polarization along the *c*-axis) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films.

strates. In these studies we have observed small changes in crystal orientation for anisotropic high- T_c material that are difficult to detect by other methods such as x-ray powder diffraction and some other methods commonly used for surface analysis. With the improvement of the growth conditions and film quality, a more quantitative study can be carried out using the same method, in order to answer the questions regarding the physical mechanisms responsible for the orientation changes with film thickness in the growth process.

IV. SUMMARY

Relative changes in the orientation of high-temperature superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films were studied as a function of film thickness using spectroscopic polarization modulation ellipsometry (SPME). We have used the fact that the dielectric characteristics of the material are highly anisotropic parallel and perpendicular to the *c*-axis. Therefore small changes in the film orientation that may not be detected by other methods (e.g., x ray, SEM etc...) can be detected by SPME measurements due to the large difference in the optical response of the films along different directions. We have observed that the decrease in metallic dielectric behavior associated with the increase in the thickness of the films grown on (100) SrTiO_3 substrates is mainly due to a change in the orientation of the

films. Also, we have found that for our films, the orientation changes more significantly for films grown on (100) SrTiO₃ than it does for films grown on (110) SrTiO₃. Therefore, we have demonstrated that SPME can be utilized as a highly sensitive nondestructive optical method for investigating the relative crystal orientation as a function of film thickness for YBa₂Cu₃O_{7- δ} films.

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