EFFECTS OF ETCHING ON THE MORPHOLOGY AND SURFACE RESISTANCE OF $YBa_2Cu_3O_{7-\delta}$ FILMS

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Abstract **- The changes in surface morphology and surface resistance of sputtered and laser ablated $YBa_2Cu_3O_{7-\delta}$ films both before and after etching have been examined. Six different etchants were used: citric acid, nitric acid, Br-methanol, EDTA, disodium EDTA, and ion milling. The surface morphologies of the films were examined by reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM), both before and after etching. The surface resistance (R_s) was measured at 94 GHz using a confocal resonator. An amorphous layer was found on the film surfaces after exposure to air. A few of the etches restored some of the surface crystallinity, but most caused increases in the overall surface roughness. Several of the wet etches attacked dislocations. Ion milling caused the largest degradation of surface crystallinity and a corresponding increase in R_s. Some of the chemical etches increased R_s by less than 15%.**

I. INTRODUCTION

High temperature superconductors have demonstrated considerable potential for use in a wide variety of high frequency and Josephson applications. Many of these devices require processing of the superconductor film to form fine features. Well controlled etches, which do not adversely affect superconducting parameters, such as surface resistance (R_s) or transport critical current density (J_c), and which selectively etch the superconductor are desired for fabrication of these small features. In addition it is important to be able to maintain or obtain clean surfaces during processing for the formation of contacts, junctions and microwave structures.

Several studies have been performed of the influence of various etches on the surface resistance of high temperature superconductor thin films[1]-[4]. However, none have reported on how the etching affects the topographies of the films. We report here on the influence of several different etches on both the surface resistance and the surface morphologies of $YBa_2Cu_3O_{7-\delta}$ thin films.

II. EXPERIMENTAL PROCEDURE

Thin films of $YBa_2Cu_3O_{7-\delta}$ were deposited on $LaAlO_3$ substrates by off axis dc magnetron sputtering. The dc power was fixed at 110 W (120 V). The substrate temperature was 735°C, and the total gas pressure was 12 Pa (90 mTorr), made up of 50% Ar and 50% O_2. The films were grown to thicknesses of 400 nm at a deposition rate of 40 nm/h.

The surface morphologies of the films were examined by atomic force microscopy (AFM) and reflected high energy electron diffraction (RHEED). AFM was performed under ambient conditions with chemically sharpened Si tips. RHEED patterns were taken of the films after they had been exposed to ambient conditions for several weeks and again after the films were etched. RHEED analyses were performed at room temperature with an incident electron energy of 20 keV and an incident electron angle of 1°. Both the (100) and the (110) reflections of the films were examined.

Microwave surface resistance measurements were performed using a confocal resonator at 94 GHz and 77 K. This technique measures the central 5 mm of the superconductor surface and is more fully described elsewhere[5]. Films were measured both before and after etching.

Six different etchants were used: 0.1 vol.% nitric acid in deionized water, 0.001 M citric acid in deionized water, 1 vol.% Br in methanol, saturated ethylenediaminetetraacetic acid (EDTA) in deionized water, saturated disodium EDTA in deionized water, and a 300 V ion beam. The etching rate of each etchant was determined on several $YBa_2Cu_3O_{7-\delta}$ films prior to use on the samples described here. Etching times were chosen to remove 20 nm of the $YBa_2Cu_3O_{7-\delta}$ films. After etching the samples were rinsed in deionized water, blown dry with nitrogen, and immediately put into the vacuum chamber for RHEED analysis.

III. RESULTS AND DISCUSSION

A. Atomic Force Microscopy

AFM images of the as deposited films reveal morphologies with many square features (Fig. 1.) It is likely that these features correspond to the spiral growth features imaged on other sputtered $YBa_2Cu_3O_{7-\delta}$ films by scanning tunneling microscopy[6]-[8]. The AFM does not image the spiral growth features due to the reacted layer on the film surfaces[9]. In addition the surfaces appear to be covered with small particles. These particles have been observed on $YBa_2Cu_3O_{7-\delta}$ films grown by a variety of techniques[10]. The morphologies of all the films studied here were very similar. All had square

Manuscript received October 17, 1994.

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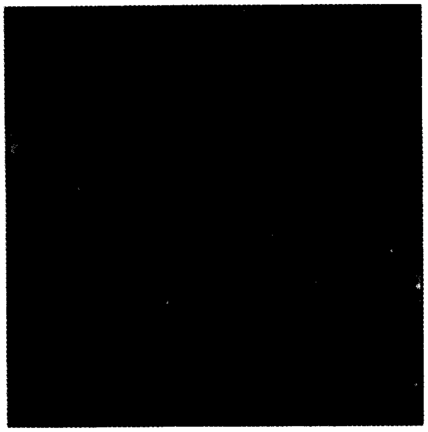

Fig. 1 AFM image of an as deposited $YBa_2Cu_3O_{7-\delta}$ film on $LaAlO_3$. The image is 2.5 x 2.5 μm^2 and the gray scale is 10nm.

features of the same size and density. None contained long rectangular grains suggesting a-axis growth; however, a few had small pinholes.

The rates of film removal determined for the various etches are given in Table I. The morphologies of the etched films, as imaged by AFM, are shown in Fig. 2. Each image is of a 1 μm x 1 μm area; however, the gray scales for the images differ, as described in the caption.

The ion milled sample (Fig. 2 a) shows the least change in surface morphology; in fact the topography is virtually identical to that imaged for the film prior to milling, both in lateral feature size and vertical surface roughness. This is consistent with ion milling being a very uniform process for material removal.

Several of the etches, citric acid, nitric acid and disodium EDTA (fig. 2 b,c,d), appear to preferentially etch pits into the $YBa_2Cu_3O_{7-\delta}$ films. The shape of the pits suggests etching of dislocations. However, it is not clear whether the dislocations being etched are at the center of spiral growth features, or at intersections where the growth features coalesce. Of these etches, the citric acid appears to have the most preferential attack of the dislocations. The film etched with citric acid (Fig. 2 b) has the most and deepest etch pits, while the regions of the film between the etch pits closely resemble the unetched film morphology without the relief of the square growth features. The films etched with nitric acid and disodium EDTA etches also have dislocation etch pits, but they are fewer and shallower. On these films as well, the regions between the pits are similar to the small scale surface roughness of the as deposited films, although the features on the film etched with disodium EDTA are the least distinct. Actually the surface roughness between the dislocations on all three films is less than that of the original as-deposited films because the roughness of the square growth features has been removed.

The preferential attack of these acid etches for the square growth features and the dislocations indicates an anisotropy in the etching along different crystallographic directions in $YBa_2Cu_3O_{7-\delta}$. The etches attack the sides of the square growth features and remove the free standing layers until a flat continuous (001) $YBa_2Cu_3O_{7-\delta}$ surface is exposed and there are no (100) or (010) surfaces left to etch. This may make these etches useful for etching side walls. However, the etch pits formed with the citric acid are very deep, indicating that it rapidly attacks defective material as well. The nitric acid and disodium EDTA etches have similar effects, but to lesser extents. This anisotropic etching means that the rates determined for these etches (see Table I) are only approximate.

TABLE I

Etch	Etch Rate(nm/s)
Ion mill 300V, 0.12 mA/cm^2	0.05±0.001
Citric Acid 0.001M	0.6±0.2
0.1% HNO_3	1.3±0.2
DiSodium EDTA (saturated)	0.22±0.03
EDTA (saturated)	2.4±0.1
1% Br in methanol	1.15±0.06

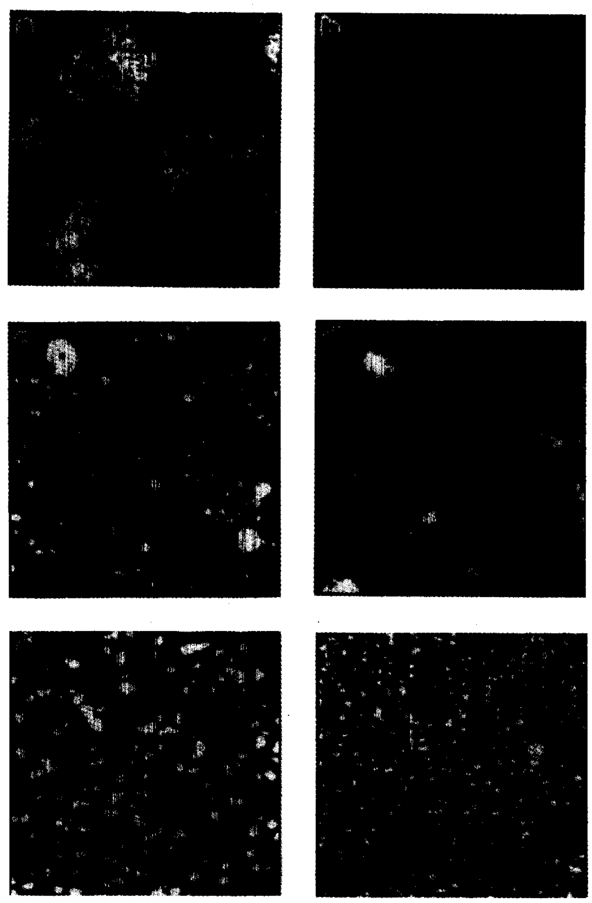

Fig. 2 AFM images of the $YBa_2Cu_3O_{7-\delta}$ films after etching with: a)ion mill, b) citric acid, c)nitric acid, d)disodium EDTA, e)EDTA, and f)Br:methanol. Each image is 1 μm^2; the gray scales are 10, 120, 10, 10, 50, and 20 nm respectively.

The roughest surface, without etch pits, was produced by the EDTA etch without sodium. The surface of the EDTA etched film (Fig. 2 e) has many granular features, ~50 nm in diameter, which is larger than those present on the original film surface. The surface roughness is on the order of the granular feature size, and is several times larger than that of the as deposited film. The film etched with Br:methanol solution has a similar granular surface (Fig. 2 f). Although the particle size, 25 nm, and surface roughness of this film are smaller than those of the EDTA etched film they are larger than those of the as deposited surface.

B. Reflected High Energy Electron Diffraction

A RHEED pattern of a (110) reflection from a laser ablated $YBa_2Cu_3O_{7-\delta}$ film taken *in-situ* in the deposition chamber immediately after deposition is shown in Fig. 3 a. Although this film was laser ablated rather than sputter deposited, STM images showed spiral growth features on a scale similar to those observed on the films used in this study. The pattern is included to show that the as deposited films produce strong reflected streaks, indicating highly crystalline two dimensional surfaces.

After the sputtered films had been exposed to ambient conditions for several weeks, but prior to etching, RHEED analyses revealed diffuse background scattering, without any diffracted patterns (Fig. 3 b). This is due to the amorphous phase on the surface of the $YBa_2Cu_3O_{7-\delta}$ caused by reaction with the atmosphere[9]. A few of the patterns from air exposed films also contained rings (similar to those in Fig. 3 d). The source of these rings must be randomly oriented particulates which protrude above the film surface to produce transmitted diffraction. These are probably a second phase on the surface of the films, possibly the small particles imaged by AFM.

After etching, the three films which had dislocation etch pits (those etched with citric acid, nitric acid and disodium EDTA, see Fig. 2 b,c,d) showed some surface crystallinity by RHEED (Fig. 3 c). The fact that the patterns show spots rather than uniform streaks is probably a result of the three dimensionality caused by the etch pits.

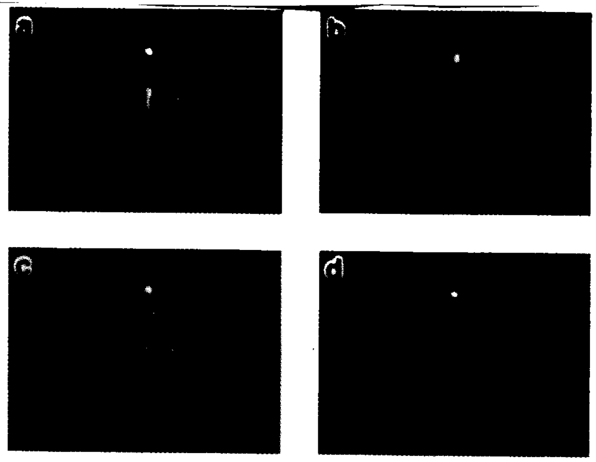

Fig. 3 RHEED patterns of $YBa_2Cu_3O_{7-\delta}$ films: a)in-situ immediately after deposition, b)after exposure to ambient conditions, c)etched with citric acid, and d)etched with Br:methanol.

The film which appeared the roughest by AFM, that etched with EDTA, showed only rings. It may be that the small particles observed on the surface of this film are randomly oriented grains of an unidentified second phase. The film etched with Br:methanol solution, which appeared similar to that etched with EDTA, but with smaller particles, also produced rings in the RHEED pattern (fig. 3 d). In addition it showed weak diffraction spots with the appropriate spacing for $YBa_2Cu_3O_{7-\delta}$. These spots probably result from transmission through regions of the oriented $YBa_2Cu_3O_{7-\delta}$ film with large surface roughness.

The pattern for the ion milled sample showed only diffuse background, indicating that any crystallinity in the surface region had been destroyed.

C. Surface Resistance

The results of the surface resistance measurements before and after etching are given in Table II. The values given are

TABLE II

Etch	time (s)	Morphology	RHEED after etch	R_s(mΩ) before etch	R_s(mΩ) after etch
Ion mill 5 run average*	360	unchanged	diffuse	40 63±23	70 85±38
.001M citric acid	33	etch pits	weak spotty streaks	40	63
0.1% HNO_3 2 run average*	15	etch pits	weak spots	45 46±2	100 75±25
Disodium EDTA	100	etch pits	weak spots	131	110
EDTA 5 run average*	10	~50 nm particles	rings	84 62±18	64 62±17
1%Br in Methanol	18	~25 nm particles	diffuse rings, weak spots	51	55

R_s data at 94 Ghz and 77 K for etched YBCO thin-films.
* denotes runs were performed using different etch times and conditions.

accurate to within 15%. Before etching, the films were of good quality with low R_s. For several of the etches more than one film was etched and measured. For these, the first values given correspond to the films for which AFM and RHEED data are shown here. A wide range of surface resistance values and changes in R_s were measured.

Except for two films which did not change within the accuracy of the measurement, all the ion-milled samples showed an increase in R_s. This is probably due to the damage to the crystal structure revealed by RHEED. The amount that R_s increases probably depends on the depth of the damage, which was not measured here.

A fairly large increase in surface resistance was also found for the sample etched with citric acid. This is probably due to the large etch pits which extend ~100 nm into this film.

The results for the other etches are less conclusive. Large increases in the surface resistance of films etched with nitric acid have been reported previously[4]. In this study, one film showed a large increase in R_s, while another showed no change within the accuracy of the measurement. The film etched with Na_2 EDTA also showed no change within the accuracy of the measurement. This contradicts previous reports [2,3] of increases in surface resistance of both TlBaCaCuO and $YBa_2Cu_3O_{7-\delta}$ films after etching with Na_2 EDTA and EDTA. The EDTA etched films studied here did not change within the accuracy of the measurements, except one which showed a decrease in R_s after etching. The film etched with Br:methanol also did not change within the accuracy of the measurement, although a previous study [4] found that R_s decreased after etching in Br:methanol.

IV. Summary

Different etches were found to result in different surface morphologies and degrees of crystallinity. The results of the RHEED analyses correlate well with the changes observed by AFM. For the samples with the largest changes in crystallinity (ion milled) and surface morphology (citric acid etched), corresponding increases in surface resistance were also observed. However, for most of the samples any changes in R_s went undetected, because they were less than the accuracy of the measurement (15%).

Acknowledgments

The authors thank Jack Ekin for the use of the RHEED system. The authors also acknowledge the support of ARPA.

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