IN SITU REAL-TIME STUDIES OF OXYGEN INCORPORATION IN COMPLEX OXIDE THIN FILMS USING SPECTROSCOPIC ELLIPSOMETRY AND ION SCATTERING AND RECOIL SPECTROMETRY*

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In situ Real-Time Studies of Oxygen Incorporation in Complex Oxide Thin Films using Spectroscopic Ellipsometry and Ion Scattering and Recoil Spectrometry

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ABSTRACT

The surface termination of c-axis oriented $YBa_2Cu_3O_{7-\delta}$ (YBCO) and the oxygen incorporation mechanism has been investigated using a unique combination of spectroscopic ellipsometry (SE) and time of flight ion scattering and recoil spectrometry (ToF-ISARS). The high surface sensitivity of the ToF-ISARS technique combined with the bulk oxygen sensitivity of SE are shown to yield complimentary information. The SE provided the film orientation and quality, while ToF-ISARS supplied surface compositional and structural information and enabled isotopic ^{18}O tracer studies. It was determined that the O content of the film had little effect on the surface termination of the film, indicating a lack of labile Cu(1) sites at the c-axis oriented YBCO surface. Also, strong evidence for a Ba or BaO terminated structure is shown. The data related to the ^{18}O tracer studies indicate that O from the reaction ambient incorporates only into the labile Cu(1) sites during both deposition and annealing, while stable O sites were populated with O from the sputtered target, indicating either the need for sputtered atomic O or sputtered YCuO complexes to occupy the stable Cu(2) sites.

INTRODUCTION

Complex oxide materials in thin film form exhibit appropriate properties for use in technologies such as high K DRAM capacitors, Josephson junctions, SQUIDS, and ferroelectric devices. The properties of these films have shown a critical dependence on their oxygen content, such as loss of the superconducting properties by $YBa_2Cu_3O_{7-\delta}$ (YBCO) depending upon the exact oxygen content, and the lowering of the dielectric constant of the high K material $BaSrTiO_3$ (BST) under oxygen depleted conditions. The objective of this study is to elucidate the mechanism of oxygen incorporation, as well as the structural implications using real time, *in-situ* spectroscopic ellipsometry (SE) and time-of-flight ion scattering and recoil spectrometry (ToF-ISARS). It has been shown that oxygen incorporation into complex oxide thin films can be followed in real time using SE[1,2], and that chemical and structural information such as oxygen adsorbtion and bonding sites are obtained using the ToF-ISARS techniques[3]. These complementary techniques are applied in real-time, and as such yield a wealth of information not only about the incorporation of oxygen, but also about the mechanism and structural effects relative to film function.

The oxygen in- and out-diffusion within the YBCO film, and the unit cell sub-structure of these films have been studied thoroughly by many groups (see for examples ref's 1-7). While there are some minor differences in the anisotropic diffusion constants reported, the mechanisms of diffusion are generally agreed upon [6,7]. Furthermore, there is agreement that the copper atoms within the YBCO unit cell occupy two distinct chemical environments (Figure 1), the Cu(1) "planes" of CuO containing the labile O , the Cu(2) "chains" of CuO being stable, while the O occupying the site joining the two becomes partially vacant in the early stages of O loss, only to return upon the phase transition from orthorhombic to tetragonal (O-T, δ>.65)[8]. Few experiments have been done concerning the film growth and oxygen incorporation mechanisms[9,10], and surface termination[11,12], the latter yielding either a BaO or CuO terminated layer, depending upon the techniques used in the investigation.

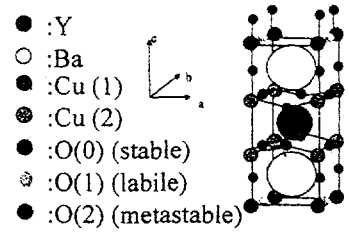

Figure 1 YBCO unit cell

EXPERIMENTAL

Thin film growth of YBCO was accomplished via a reactive ion beam sputter deposition system previously described elsewhere[3,13] . YBCO was sputtered in a 10^{-4} torr ambient of O_2 gas and allowed to deposit on a <100> single crystal MgO substrate, followed by cooling in an O_2 ambient of up to 10^{-3}torr. The orientation of the film was controlled via substrate temperature during deposition, and verified using both SE[3,14,15] and Ion Scattering [13] data. Oxygen content of the YBCO film was varied by annealing the film at 500^{0}C in background pressures of 10^{-7} – 10^{-3} torr O_2.

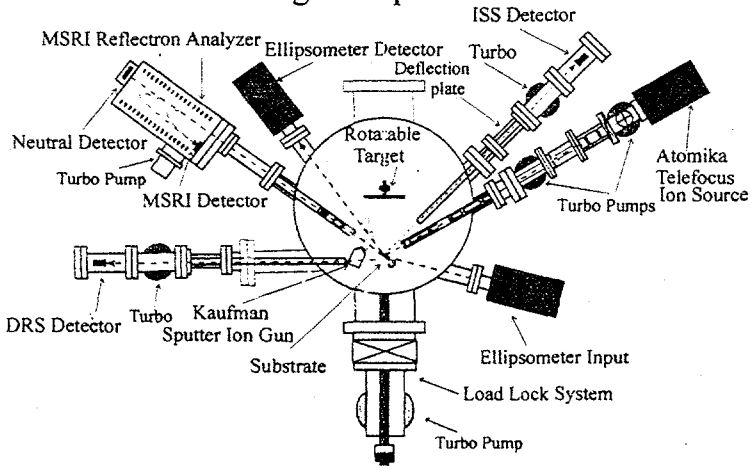

Figure 2 Deposition/ Analysis geometry

Two films of different orientation were deposited. The first was grown under our normal conditions at a deposition temperature of 750^{0}C, using O_2 background gas of normal isotopic abundances (hereby referred to as $^{16}O_2$), yielding a c-axis oriented O-rich film. The next was deposited at lower temperature (~650^{0}C) to yield an a-b oriented film. Deposition in this case was done in an ambient of 99.99% $^{18}O_2$, in order to trace the background O incorporation into the film. Each film was subsequently annealed in $^{16}O_2$ and $^{18}O_2$ to observe the exchange of labile O within the lattice.

Analysis of the resulting films was done in real-time using a unique geometry incorporating both ToF-ISARS and SE (Figure 2). Forward and backscatter spectra, using

62° and 165° scattering angles, respectivey, allowed to determine the surface structure, while the relative changes in the surface concentration of O was monitored using mass spectrometry of recoiled ions (MSRI) collected at a recoil angle of 62^0. The overall O content of the films was monitored via the 4.1eV absorbtion peak[1,2] in the SE spectra.

RESULTS AND DISCUSSION

MSRI and ISS spectra taken for the normal O_2-vacuum anneal cycle of YBCO (Figure 3) provide evidence for an increase in the surface O/Cu ratio as seen by a comparison of Fig. 3a and 3b. SE spectra shown in Figure 4a show that the bulk film is O deficient after the vacuum anneal. This would indicate that the surface is not the

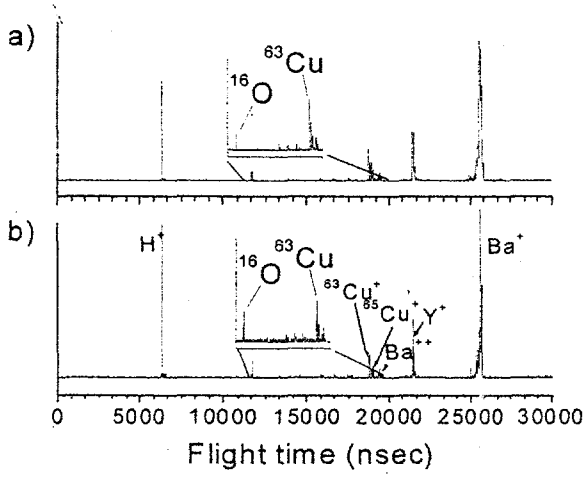

Figure 3 MSRI of a) O rich b) O deficient YBCO

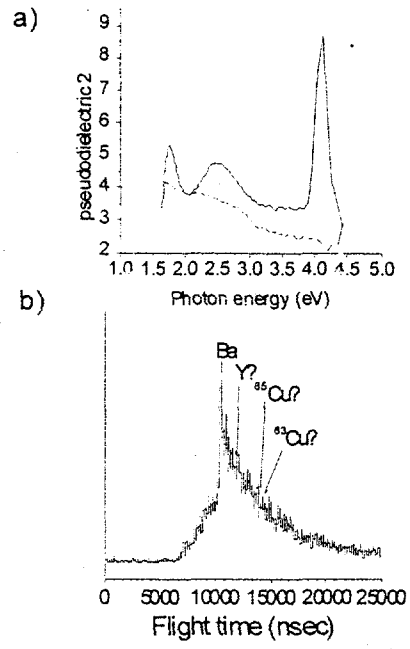

Figure 4 a) SE of O rich (dashed) and O deficient (solid) films b) Backscatter spectra of O deficient YBCO

Cu(1) plane with labile O. In addition the surface is seen to contain an abundance of Ba as evidenced in both the recoil and scattering spectra (Figures 3 and 4b). The data presented above indicate that the c-axis YBCO film has a Ba-terminated surface.

Annealing the sample in a 10^{-4} torr $^{18}O_2$ ambient revealed that although there is surface adsorbtion of O, the O signal drops dramatically immediately upon the removal of the oxygen ambient (Figure 5). Furthermore, the MSRI signal of ^{18}O is considerably lower than the ^{16}O signal, indicating that the O sites closest to the surface must be the stable CuO chains or the BaO plane.

The a-b oriented YBCO film grown in an ambient of $^{18}O_2$ indicates that the incorporation of O into the different sites occurs by different mechanisms. The ^{16}O signal in this film must originate from the stoichiometric YBCO target, which contains O in its

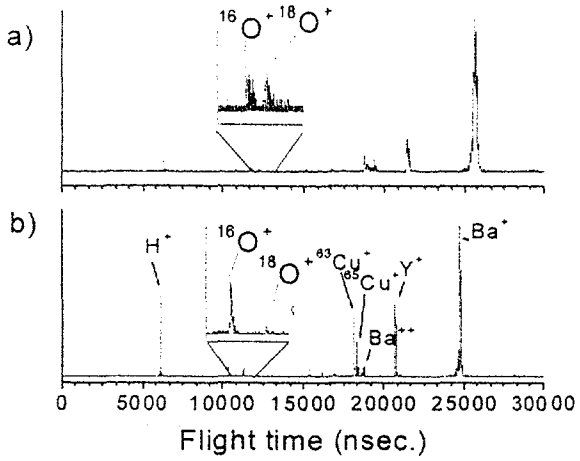

Figure 5 MSRI of $^{18}O_2$ annealed YBCO a) 10^{-4} torr $^{18}O_2$ b) in vacuum

CONCLUSIONS

An understanding of O content in complex oxide thin-film systems is tantamount to understanding most of the important properties of these materials. The O incorporation mechanism for YBCO films, both in terms of the surface composition and structure, has been elucidated using a. combination of SE and ToF-ISARS in real-time studies

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natural isotopic abundance. The complete disappearance of the ^{18}O MSRI signal upon annealing of this film, indicates that the ambient O is incorporated only into the labile O sites, while the stable CuO chains are the result of either sputtered elemental O or YCuO complexes[8,9]. The increase in the ^{18}O signal in the as deposited film as compared to the $^{18}O_2$ annealed film is a function of the film orientation, as the first non-surface layer of labile O is located two layers closer to the surface than in the c-axis oriented film.

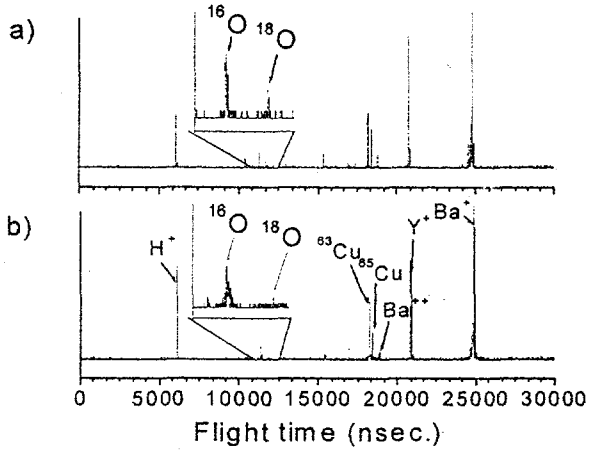

Figure 6 MSRI of YBCO deposited in $^{18}O_2$ ambient a) as deposited b) $^{16}O_2$ annealed

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