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

A. H. Mueller¹, Y. Gao¹, E. A. Irene¹, O. Auciello², A. R. Krauss³, and J. A. Schultz⁴

¹University of North Carolina
Dept. of Chemistry
Chapel Hill, NC

²Materials Science Division
³Chemistry Division
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439

⁴Ionwerks
Houston, TX

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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

A.H. MUELLER, Y. GAO, E.A. IRENE
O. AUCIELLO*, A.R. KRAUSS*
J.A. SCHULTZ**
Department of Chemistry, University of North Carolina at Chapel Hill
* Material Science and Chemistry Division, Argonne National Laboratory
** Ionwerks Inc., Houston, Texas

ABSTRACT

The surface termination of c-axis oriented YBa$_2$Cu$_3$O$_{7-\delta}$ (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$_2$Cu$_3$O$_{7-\delta}$ (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 adsorption 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 substructure 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 \(^6\). 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, \(\delta>.65\))\(^8\). 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.

**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 \(500^\circ C\) in background pressures of \(10^{-7} - 10^{-3}\) torr \(O_2\).

Two films of different orientation were deposited. The first was grown under our normal conditions at a deposition temperature of \(750^\circ C\), 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°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, respectively, 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°. The overall O content of the films was monitored via the 4.1 eV absorption peak in the SE spectra.

RESULTS AND DISCUSSION

MSRI and ISS spectra taken for the normal O₂-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 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 ¹⁸O₂ ambient revealed that although there is surface adsorption of O, the O signal drops dramatically immediately upon the removal of the oxygen ambient (Figure 5). Furthermore, the MSRI signal of ¹⁸O is considerably lower than the ¹⁶O 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 ¹⁸O₂ indicates that the incorporation of O into the different sites occurs by different mechanisms. The ¹⁶O signal in this film must originate from the stoichiometric YBCO target, which contains O in its...
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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REFERENCES