STUDIES OF METALLIC SPECIES INCORPORATION DURING GROWTH OF $SrBi_2Ta_2O_9$ FILMS ON $YBa_2Cu_3O_{7-x}$ SUBSTRATES USING MASS SPECTROSCOPY OF RECOILED IONS

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DISCLAIMER

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ABSTRACT

The incorporation of metallic species (Bi, Sr and Ta) during the growth of layered perovskite $SrBi_2Ta_2O_9$ (SBT) on a-axis oriented $YBa_2Cu_3O_{7-x}$ (YBCO) conducting oxide substrates has been investigated using *in situ* low energy mass spectroscopy of recoiled ions (MSRI). This technique is capable of providing monolayer-specific surface information relevant to the growth of single and multi-component thin films and layered heterostructures. The data show a temperature dependence of metallic species incorporation during co-deposition of Sr, Bi and Ta on YBCO surfaces. At high temperatures ($400 < T \leq 700^{\circ}C$), negligible incorporation of Bi is observed as compared to Ta and Sr. At low temperatures ($\leq 400^{\circ}C$), there is a substantial incorporation of Bi, Sr and Ta on the surface of YBCO, and the MSRI signal intensities for Sr, Bi and Ta are nearly independent of substrate temperature. According to thermodynamic calculations, the presence of Ba and Y on the YBCO surface inhibit the incorporation of Bi due to competition for oxygen required to establish bonding of metallic species to the surface. This may be the explanation for the observed Bi deficiency in films grown on YBCO surfaces at temperatures > 400 °C. SBT films grown at temperatures ≤ 400 °C and annealed in oxygen or air at 800 °C exhibit a polycrystalline structure with partial a-axis orientation.

INTRODUCTION

In order to understand and control the synthesis and resulting microstructure and properties of SBT thin films on different substrates, it is necessary to perform a systematic investigation of the effect of growth parameters and techniques on the composition, microstructure and properties of SBT layers using different electrode materials. One of the objectives of studying the synthesis of SBT films on electrode layers with controlled structure is to investigate the possibility of maximizing the polarization of SBT capacitors through control of the SBT layer orientation. Most SBT capacitors produced until now contain polycrystalline SBT layers, such that the maximum polarization of the SBT capacitors is much smaller (~ 11-12 $\mu C/cm^2$)[1] than for PZT capacitors with highly c-axis oriented PZT layers, which exhibit polarization of up to 40-50 $\mu C/cm^2$.[2,3] It has been determined that the direction of maximum polarization in SBT layers is parallel to, or at an angle close to the a-b plane.[4] Therefore, the purpose of the present work is to study the growth of SBT films on a-axis oriented conductive $YBa_2Cu_3O_{7-x}$ (YBCO) electrode layers in order to investigate the possibility of using a-axis oriented YBCO as

a template layer to induce the growth of a-axis oriented SBT films, which may exhibit enhanced polarization. During the growth studies of SBT films on YBCO, interesting effects regarding the incorporation of species like Bi and Ta on the YBCO surface were noted. In previous studies,[5] we investigated the incorporation of metallic species in sputter-deposited SBT films on Pt/Ti electrode layers. Those studies revealed that Ti segregated to the surface of the Pt layer when heating the Pt/Ti heterostructure to the 400-700°C temperature range. The segregated Ti species inhibited the incorporation of Bi in the initial stages of the SBT layer growth, due to the competition for oxygen with the depositing Bi species.[5] In the present work, we have investigated the effect of growth temperature, and of the a-axis oriented YBCO electrode surface on the incorporation of metallic species in a growing SBT film.

EXPERIMENTAL APPROACH

The investigation of growth processes in the present work has been conducted using a unique Mass Spectroscopy of Recoiled Ions (MSRI) technique recently developed in an Ionwerks-Argonne National Laboratory collaboration.[6,7] MSRI provides a unique diagnostic capability for thin film growth processes of multicomponent oxides. MSRI is one of the three modes of operation of a generic time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) technique capable of providing insights into the growth of films under a wide range of growth conditions. The technical and operational details of TOF-ISARS can be found in earlier publications.[5-7]

In the present work, ion beam sputter deposition has been employed to grow SBT thin films on a-axis oriented YBCO layers produced by pulsed laser ablation deposition on $LaAlO_3$ (LAO) substrates. The SBT films were deposited at substrate temperatures in the 20-700°C range, in 5 x 10^{-4} Torr of oxygen, using 500 eV Xe^+ ion beam sputtering of a stoichiometric $SrBi_2Ta_2O_9$ target.

RESULTS AND DISCUSSION

Film growth was carried out at various temperatures ranging from 200 °C to 700 °C in an atmosphere of $5x10^{-4}$ Torr of O_2. The total amount of material deposited on the substrate was measured with a quartz crystal thin film monitor, while species incorporation was monitored via MSRI. At 700 °C, there was little attenuation of the substrate Y, Ba and Cu signals. A Ta signal was observed, which stabilized at a point corresponding to the deposition of 1500 Å of material according to the quartz crystal thin film monitor. No Bi or Sr signal was observed, although, since the Sr and Y MSRI signals overlap there may have been some Sr present. After 2000 Å of material had been deposited, the temperature was then lowered to 640 °C with little change in the spectra.

Figure 1(a) shows the MSRI spectrum obtained after an aditional 100 Å of material had been deposited at 640 °C. Ta remains the only visible peak corresponding to the deposited material, and the strong Y, Ba and Cu peaks suggest that Ta is sticking only in the form of isolated islands, possibly as TaO_2. Lowering the substrate temperature to 400 °C results in a prompt (24 Å) (Fig. 1(b)) appearance of the Bi signal, and further deposition (Fig. 1(c)) at this temperature shows little increase with deposition time.

In a separate experiment, MSRI analysis showed that during the initial stages of co-deposition of 100 Å thick layers of Sr, Bi, and Ta at substrate temperatures ranging from 700 °C

to 400 °C, there is a continuous increase in the incorporation of Sr, Bi, and Ta, with Bi showing the strongest variation, as the temperature decreases. For substrate temperatures below 400 °C, the MSRI Sr, Bi, and Ta peak intensities remain constant, indicating that the incorporation of SBT species have reached an equilibrium condition (Fig. 2).

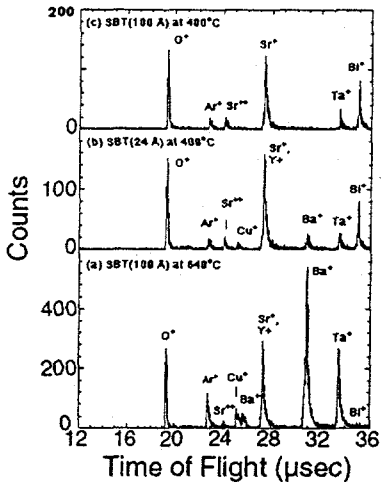

Figure 1. MSRI (+ ion) spectra corresponding to the co-deposition of Sr, Bi, and Ta species on a YBCO surface in an oxygen atmosphere: (a) 100 Å at 640°C; (b) additional 24 Å at 400°C; and (c) additional 100 Å at 400°C as the growth continues on the YBCO/LAO surface in Po_2=5x10^{-4} Torr.

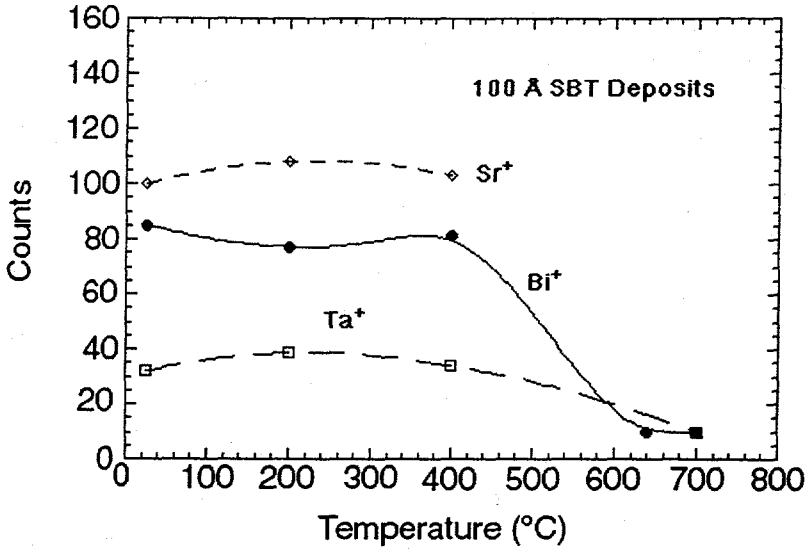

Figure 2. Temperature dependence of the incorporation of Bi, Ta and Sr species during the initial growth of SBT on an YBCO surface under Po_2=5x10^{-4} Torr.

Figure 3 shows the evolution of the MSRI peak intensities shown in Fig. 1 at various substrate temperatures. The x-axis corresponds to the incremental film thickness measured by the thin film monitor after the reduction in substrate temperature to 640 °C, as described above. At 640°C, the MSRI peak intensities corresponding to Y^+, Ba^+, Cu^+ (of the YBCO layer), and Sr^+ and Ta^+ (of the Bi-deficient SBT film) remain constant and the Bi^+ peak intensity is very small. However, as soon as the substrate temperature is reduced to 400°C, a substantial increase in the Bi^+ signal is clearly seen. The increased Bi^+ signal at 400°C correlates with a drop in the MSRI peak intensities of Ba^+, Y^+, and Cu^+. As the film continues to grow, the Ba^+, Y^+ and Cu^+ signals disappear completely and the Bi^+, Sr^+ and Ta^+ signals stabilize, corresponding to the formation of a continuous film. Further decrease in the growth temperature to 200°C, results only in a small increase in the incorporation of Bi and Ta in the growing film. At temperatures lower than 200°C, incorporation of the Sr, Bi, and Ta metallic species remains constant.

The free energies of oxide formation ($\Delta G_f^{o)}$) were calculated using standard coefficients in the free energy equation[8] and are plotted as a function of temperature in Figure 4. Note that there are two curves for Bi, corresponding to two different oxidation states. The values for Ba,

Sr, Y and Ta are lower than that of both of the Bi oxidation states over the entire temperature range shown in the figure. Bi, Sr and Ta are co-deposited as metallic species that are quickly stabilized at the surface as simple oxides, with subsequent annealing to form the SBT crystal structure. If there is an inadequate oxygen background pressure during this annealing period, or if the substrate effectively competes with the deposited metallic species for the available oxygen, the simple oxides will be oxygen deficient. YBCO is known to be oxygen-deficient at elevated

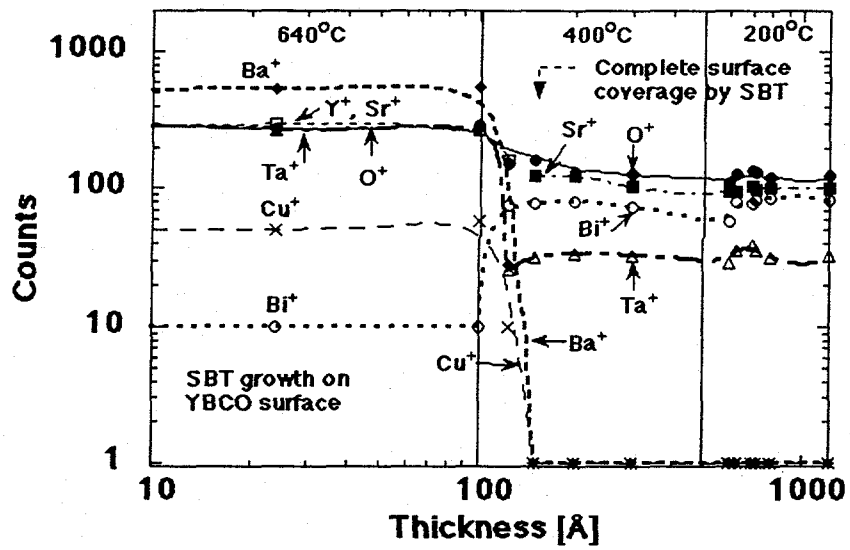

Figure 3. Variations in the MSRI signals for metallic and oxygen species as a function of film thickness during the co-deposition of Sr, Bi, and Ta species on a YBCO surface under $Po_2=5x10^{-4}$ Torr. There is a complete surface coverage at ~50 Å of film growth at 400°C.

temperatures and low oxygen pressure atmospheres.[9] Under these conditions, the substrate elements are therefore not oxygen-saturated and may compete with the Sr, Bi, and Ta species for the available oxygen. Bi is simultaneously the most volatile elemental species and the species with the highest heat of oxide formation. It is therefore expected that Bi is unable to compete for the available oxygen and therefore evaporates at high substrate temperatures. Both Ba and Y have lower heats of oxide formation (larger magnitude) than that of Bi and are therefore capable of reducing the Bi oxides to elemental Bi via the following reactions.

$$3Ba + Bi_2O_3 = 3BaO + 2\ Bi\ ;\ \Delta G_f^\circ\ (640^\circ C) \approx -35.42\ kCal/mole \quad (1)$$

$$2Y + Bi_2O_3 = Y_2O_3 + 2\ Bi\ ;\ \Delta G_f^\circ\ (640^\circ C) \approx -275.91\ kCal/mole \quad (2)$$

$$Ba + BiO = BaO + Bi;\ \Delta G_f^\circ\ (640^\circ C) \approx -84.72\ kCal/mol \quad (3)$$

$$2Y + 3BiO = Y_2O_3 + 3\ Bi\ ;\ \Delta G_f^\circ\ (640^\circ C) \approx -325.20\ kCal/mole \quad (4)$$

Y is clearly the dominant species in the competition with Bi for oxygen at all temperatures. However, as the substrate temperature is lowered, the evaporation rate of elemental Bi decreases, and the YBCO becomes more fully oxygen-saturated, and therefore less effective in reducing the bismuth oxides to elemental Bi. The results obtained in this work are in agreement with prior experiments[5, 10] that demonstrated that sputter-deposited SBT films can be efficiently grown on surfaces containing species with small ΔG_f° values (e.g., Ti and/or Si) only when the substrate temperature is ≤ 400 °C.

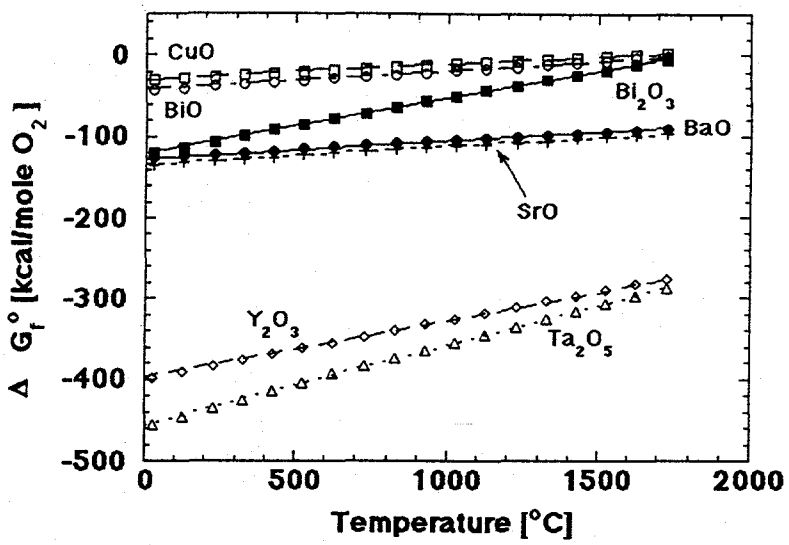

Figure 4. Free energy of formation of oxides as a function of temperature.

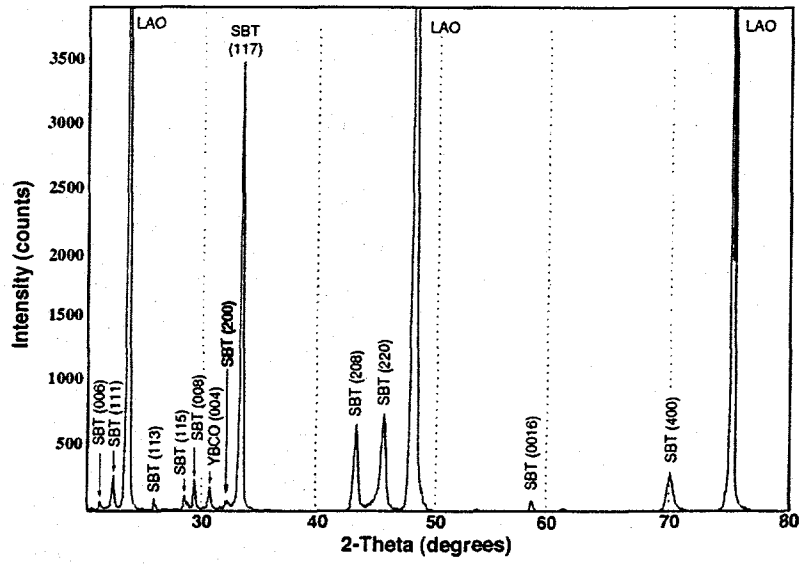

Figure 5. XRD spectrum of a polycrystalline sputter-deposited SBT film grown on an a-axis oriented YBCO surface at ≤ 400 °C and subsequently annealed in oxygen at 800 °C. Notice the (400) and (200) peaks which reveal that the SBT film has partial a-axis orientation.

Using the information obtained from the MSRI studies, we were able to grow an SBT film on an a-axis oriented YBCO substrate at temperatures ≤ 400 °C followed by an annealing step at 800 °C in oxygen. X-ray diffraction analysis revealed that the SBT film had a polycrystalline structure with partial a-axis orientation (see Fig. 5). Although, this represents a promising development, further work is necessary to identify the combined thermodynamic-kinetic conditions needed to synthesize pure a-axis oriented SBT films on substrates with appropriate orientation such as a-axis YBCO.

CONCLUSIONS

In conclusion, at high substrate temperatures ($400 < T \leq 700$ °C), there is a negligible incorporation of Bi as compared to Ta and Sr, during the SBT growth on YBCO substrates. At low temperatures (≤ 400 °C), there is a substantial incorporation of Bi on the YBCO surface. According to calculations of the free energies of oxide formation, the presence of Y and Ba on the YBCO surface inhibit the incorporation of Bi due to a competition for oxygen. Negligible Bi incorporation during high temperature growth of SBT films makes it difficult to grow stoichiometric a-axis oriented SBT films on a-axis oriented YBCO substrates. Therefore, further research is necessary, particularly the investigation of other substrates also, to determine the optimum substrate-deposition conditions for the growth of a-axis oriented SBT films.

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