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Growth of $YBa_2Cu_4O_8$ thin films from sputtered precursors and their thermal stability

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The growth of $YBa_2Cu_4O_8$ (Y124) thin films from several kinds of precursors deposited at different temperatures has been studied by micro-Raman spectroscopy. The Y124 thin films were prepared through *in situ* annealing of sputtered precursors. The ratio of Raman vibrational intensity of oxygen in the double Cu-O chain to that of an apical oxygen was used to measure the volume fraction of the Y124 phase in $YBa_2Cu_3O_x$ and Y124 mixtures. The precursor preparation temperature was critical for the following growth of Y124 films. The precursors deposited below 450 °C show amorphouslike microstructures and 450 °C is the most appropriate deposition temperature. The Y_2BaCuO_5 phase or $YBa_2Cu_3O_x$ were present in the precursors deposited above 500 °C and suppressed subsequent growth of the Y124 phase. The thermal stability of Y124 films was examined by heat treatments under $0.1 \leq P_{O_2} \leq 100$ Torr, $600 \leq T \leq 800$ °C, and then compared with Y123 films. The Y124 films were stable up to 800 °C in 100 Torr O_2 and also up to 600 °C even in a reduced O_2 pressure of 1 Torr. [S0163-1829(96)03841-6]

I. INTRODUCTION

The superconducting $YBa_2Cu_4O_8$ (Y124) phase, which differs from $YBa_2Cu_3O_x$ (Y123) in that the single Cu-O chain is replaced by a double Cu-O chain, is known to have a superior thermal stability compared to the Y123 phase[1] and also has no orthorhombic-to-tetragonal phase transition.[2] Therefore, the Y124 is expected to offer some advantages in practical applications. Thin-film preparation of Y124 has been attempted by several kinds of physical vapor deposition followed by post annealing.[3–5] Relative to Y123, the Y124 phase is stable at lower temperatures and higher oxygen pressures.[6–9] These conditions require the post annealing to form the Y124 phase and make it difficult to prepare single phase films.

We have reported the preparation of dominantly a-axis oriented Y124 thin films from precursors deposited by sputtering followed by *in situ* annealing.[10,11] We have discussed the growth of the Y124 phase through solid-state reactions from several precursors deposited at substrate temperatures of 450–645 °C. We concluded that an amorphouslike precursor prepared around 450 °C is the optimum initial condition. Recently our experiments, however, showed that there was a difference in the growth of Y124 from the amorphouslike precursors deposited below 450 °C. The first goal in this study was to characterize precursors deposited below 450 °C in detail. The thick precursors (~1.2 μm) were examined by high-power x-ray diffraction and it was found that there are microstructural difference in the precursors grown below 450 °C. Since it is difficult to distinguish a-axis oriented Y124 from Y123 in x-ray diffraction because the a-lattice constants are close to each other, the Y124 films were studied by polarized Raman spectroscopy. Raman spectroscopy is effective because an energy shift of the vibration modes along the c axis in the film plane is clearly different in Y124 and Y123.

The second goal was to use Raman spectroscopy to examine the thermal stability of Y124 films in 0.1–100 Torr oxygen pressures over the 600–800 °C range. The stability of the Y124 phase has been examined by thermogravimetric measurements,[1,7,12] which demonstrated that the oxygen content of Y124 remains almost unchanged up to ~800 °C oxygen in 1 atm pressure. From the viewpoint of device preparation, it is important to determine the thermal stability of Y124 films under a low oxygen pressure or vacuum conditions. This has not been reported as far as we know.

II. EXPERIMENT

The precursors were deposited on (100) $SrTiO_3$ substrates by an off-axis magnetron sputtering using a Y124 structural target, which was described in detail elsewhere.[11,13] The precursors were deposited without heating and at 250, 450, 500, 615, 625, and 650 °C (labeled by P_{000}, P_{250}, P_{450}, P_{500}, P_{615}, P_{625}, and P_{650}). The precursor thickness was 2400 Å except for the precursors deposited below 450 °C. These were 1.2 μm thick in order to increase x-ray diffraction (XRD) intensity. The precursors were then transferred from the growth chamber to the load-lock chamber and annealed in 100 Torr O_2 at 750 °C for 1 h. Samples were heated to annealing temperature at a rate of 10 °C/min. The film prepared from a precursor P_i was referred to F_i (i=000, 250, 450,. . .).

The crystalline orientation of precursors and films was examined by XRD using a Cu $K\alpha$ source at 40 kV and 20 mA. The texture of 1.2 μm thick precursors was further examined by XRD with 40 kV and 200 mA. Micro-Raman spectroscopic measurements were performed for all the films by NR-1800 system (JASCO corporation) using a triple spectrometer and a multichannel detector. The laser beam of an excitation source of 5145 Å Ar^+ line was focused about 2 μm ϕ with a power of 0.5 mW on the films. The configuration of the polarization is $x(zz)\overline{x}$ in the Porto notation, where the direction of incoming and scattered light was perpendicular to the (100) $SrTiO_3$ with the polarization parallel to the [001] $SrTiO_3$.

For examination of thermal stability, the Y124 films prepared through *in situ* annealing (750 °C, 100 Torr O_2) from

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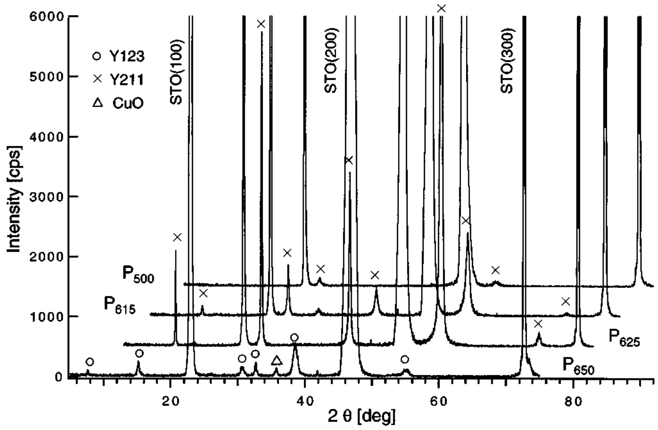

FIG. 1. XRD patterns of precursors deposited above 500 °C. Increasing the deposition temperature enhances the growth of Y211. The precursor deposited at 650 °C contains Y123 and CuO.

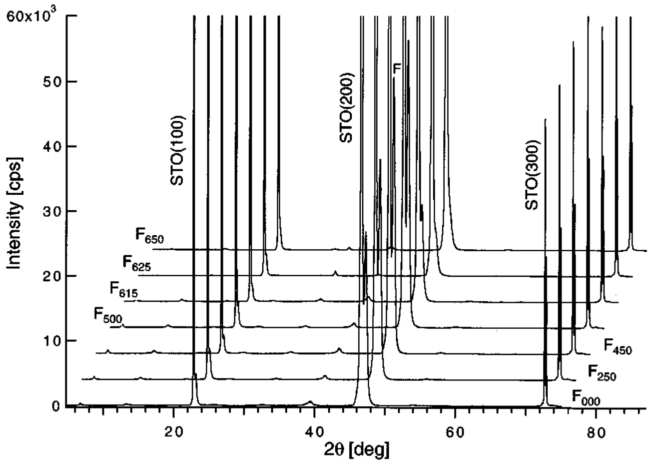

FIG. 2. XRD patterns of films grown through the *in situ* annealing of precursors deposited between RT and 650 °C. The (200) reflection labeled by ''*F*'' is discussed by means of Raman spectra as shown in Fig. 3.

precursors deposited at 450 °C were briefly exposed to the air at room temperature and heated in the load-lock chamber for 1 h in the temperature range 600–800 °C in oxygen pressures between 0.1 and 100 Torr. The heating rate was 5 °C/min. The duration of 1 h is probably long enough as Morris *et al.*[7] reported that the conversion from Y124 to Y123 around 800 °C can take place during about 1–20 min. For the comparison, *a*-axis oriented Y123 films were prepared by dc sputtering using the self-template method[14] and also annealed under the same conditions as the Y124 films.

III. RESULTS AND DISCUSSION

A. Growth of Y124 films from sputtered precursors

Figure 1 shows the XRD patterns of P_{500}, P_{615}, P_{625}, and P_{650}. The peaks marked by a cross correspond to a 7.0 Å lattice spacing perpendicular to the substrate, which has been identified[11] to be the Y_2BaCuO_5 (Y211) phase by transmission electron microscopy and scanning electron microscopy. The intensity of the Y211 peaks increase with deposition temperature. However, the Y211 phase abruptly disappears at 650 °C, and Y123 and CuO appear. All the precursors deposited below 450 °C seemed to be amorphous because no crystalline peaks were observed in the 40 kV 20 mA XRD patterns. Figure 2 shows the XRD patterns of the films grown by *in situ* annealing of the precursors. The films show *a*-axis oriented textures with the *a*-lattice constant of 3.84 Å. It is not possible to confirm the Y124 phase from the XRD patterns because the Y123 and Y124 have the *a*-lattice constant close to each other. The weak peaks are assigned to be *c*-axis oriented Y124 for samples $F_{000}\sim F_{615}$ and to be the *c*-axis oriented Y123 for samples F_{625} and F_{650}. The $x(zz)\bar{x}$ Raman spectra for the samples $F_{000}\sim F_{650}$ are shown in Fig. 3. For samples $F_{000}\sim F_{625}$, the Raman-active phonons of the Y124 phase, that is, the six A_g phonons corresponding to vibrations along the *c* axis of Y124 are identified as follows: barium (103 cm^{-1}), plane copper (149 cm^{-1}, labeled Cu_p), copper in the double Cu-O chain (250 cm^{-1}, labeled Cu_d), plane oxygen in in-phase (438 cm^{-1}, labeled O_p+), apical oxygen (495 cm^{-1}, labeled O_a), and oxygen in the double Cu-O chain (604 cm^{-1}, labeled O_d). A vibration of the plane oxygen in out-of-phase (O_p-) along the *b* axis is also observed at 333 cm^{-1}. Both modes along the *c* axis and *b* axis are observed at the same time because of the 90°-grain characteristics of *a*-axis-oriented films as observed in plan TEM view.[10] It is important that the Cu_d and O_d phonons originate from the double Cu-O chain in the Y124 phase while the other phonons are commonly observed in both of Y124 and Y123 phases.[15,16] The $a(cc)\bar{a}$ Raman spectrum of a Y124 single crystal reported by Heyen *et al.*[16] shows that the scat-

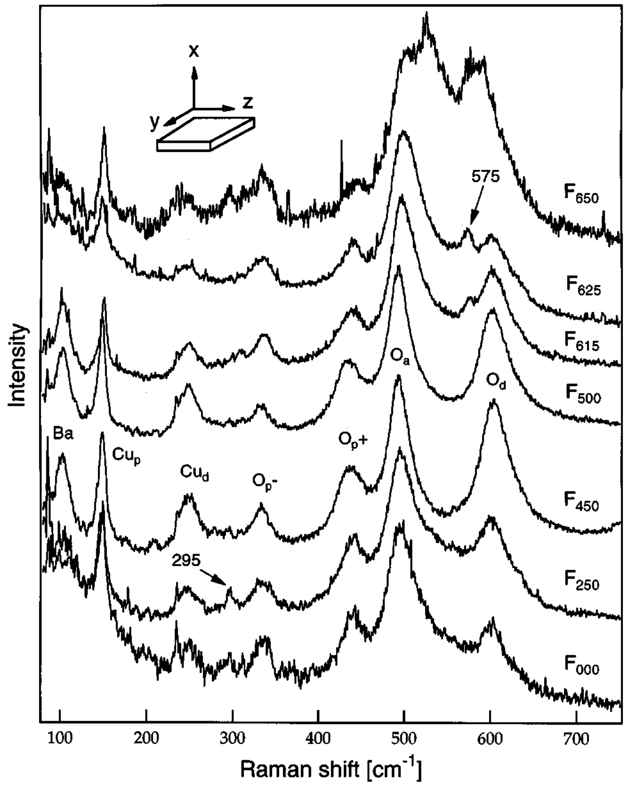

FIG. 3. The Raman spectra of the films shown in Fig. 2. The phonons at 250 cm^{-1} (Cu_d) and 604 cm^{-1} (O_d) originating from double Cu-O chains in Y124 phase are stronger in sample F_{450} than in the other samples.

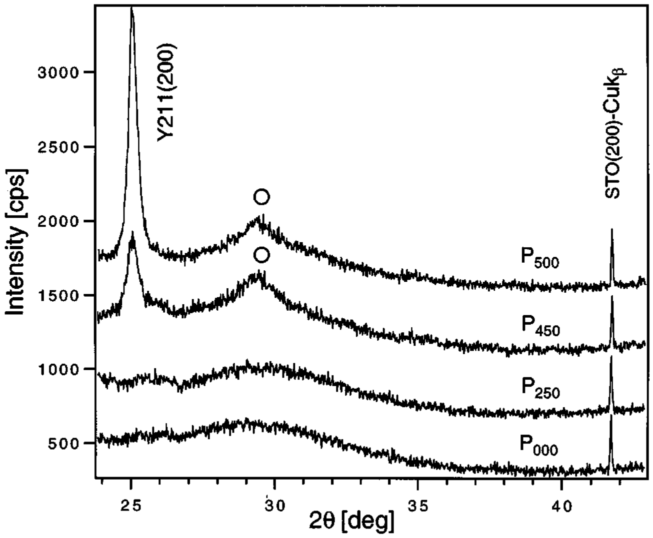

FIG. 4. XRD patterns of 1.2 μm thick precursors deposited between RT and 500 °C. The Cu $K\alpha$ source is at 40 kV and 200 mA. The broad peak indicated by an open circle is discussed in the text.

tering intensity of the O_d phonon is comparable with that of the O_a phonon. Therefore, the Raman spectrum indicates the sample F_{450} was an a-axis oriented Y124 film and the a-axis oriented peaks in the XRD patterns are confirmed to be those from the Y124 phase.

For samples $F_{450} \sim F_{625}$, the intensity of the O_d phonon in the Raman spectra and the (200) peaks in the XRD patterns decrease with increasing precursor deposition temperature. This indicates that the growth of Y124 films is suppressed by increasing the volume fraction of the Y211 phase in the precursor (see Fig. 1). The phonon at 575 cm^{-1} appearing in samples F_{615} and F_{625} has been defined to be an infrared-active mode of Y123, which is supposed to become Raman active due to oxygen defects in the single Cu-O chain.[17] The Raman-scattering spectrum for sample F_{650} does not show clear modes of double Cu-O chains. The peak for CuO is also observed at 295 cm^{-1}. The precursor P_{650} is a mixture of Y123 and CuO as shown in Fig. 1, and is found to be unsuitable for the growth of Y124 films. These are consistent with an enthalpy argument;[18] the exothermic enthalpy of conversion to Y124 from an assemblage containing Y211 is larger than that from assemblages containing Y123.

For samples F_{000}, F_{250}, and F_{450} the O_d phonon peak intensity and (200) XRD diffraction line decrease with decreasing precursor deposition temperature. For samples F_{000} and F_{250} the CuO peak is also observed at 295 cm^{-1}, which means that the films are composed of a mixture of Y124, Y123, and CuO. The samples F_{000}, F_{250}, F_{450}, and F_{500} show different crystalline structure, so we have examined precursors P_{000}, P_{250}, P_{450}, and P_{500} in more detail. The XRD patterns shown in Fig. 4 were measured at 40 kV and 200 mA and are for 1.2 μm thick $P_{000} \sim P_{500}$. The P_{450} shows a Y211 peak with lower intensity compared with the P_{500} and also shows a peak at $2\theta = 29.5°$, that is not observed in the P_{000} and P_{250}. Therefore, it is concluded that the most appropriate precursor for Y124 growth should be prepared at the lowest temperature that the Y211 growth is held to a minimum and the phase of $2\theta = 29.5°$ is contained. The lattice parameter corresponding to $2\theta = 29.5°$ is attributed to $(222)Y_2O_3$, (131)Y211, and $(600)BaCuO_2$. The thermodynamic literature[18,19] indicates that reactions involving $BaCuO_2$ as the starting material show an endothermic enthalpy change or a small exothermic one. The exothermic enthalpy change for reaction involving Y_2O_3 is larger than that for reactions including Y211 or Y123. This argument suggests that the phase of $2\theta = 29.5°$ is mainly due to Y_2O_3.

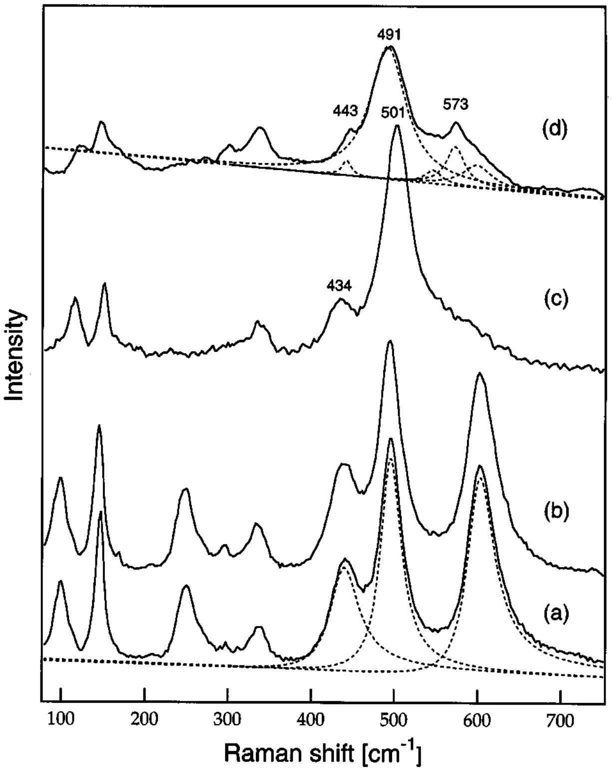

FIG. 5. The Raman spectra of (a) as-prepared Y124 film; (b) Y124 film heated at 800 °C in 100 Torr O_2 for 1 h; (c) as-prepared Y123 film; (d) Y123 film heated at 750 °C in 100 Torr O_2 for 1 h. The dotted lines represent the results fitted by Fano curves. The Y124 films show no clear variation with heat treatments, while the Y123 films show the decreasing in O_a frequency and increasing of O_p+ frequency with the appearance of 573 cm^{-1} phonon.

B. Thermal stability of Y124 films

Raman spectroscopy has been used to study the thermal stability of Y124 films in oxygen pressures of 0.1 to 100 Torr and at temperatures between 600 and 800 °C. The stability was compared with that of Y123 films. Figure 5 shows the typical change of Raman spectra of Y124 and Y123 films by heat treatment. The spectrum (b) is the result of heating of an as-prepared Y124 film (a) at 800 °C in 100 Torr O_2. The spectrum (d) is the result of heating of an as-prepared Y123 film (c) at 750 °C in 100 Torr O_2. For a quantitative discussion of the Raman spectra, each spectrum in the region of 380–780 cm^{-1} was fitted with several Fano curves as shown by dotted lines in Fig. 5. We have observed no clear variations between the spectra (a) and (b) in the Y124 films. On the other hand, in the Y123 films the spectrum (d) shows a decrease in O_a frequency and an increase in O_p+ frequency compared with (c), due to an increase in oxygen deficiency

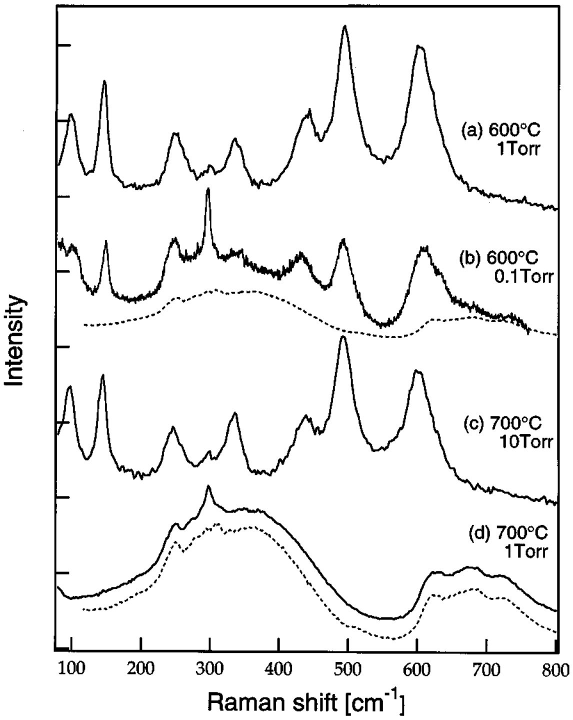

FIG. 6. The Raman spectra of Y124 films heated under the several conditions. The dotted line suggests a contribution from the substrate, $SrTiO_3$.

in the Y123 phase.[20] The peak at 573 cm^{-1} is supposed to appear due to the same reason as the phonon at 575 cm^{-1} in samples F_{615} and F_{625} in Fig. 3. These reflect the degradation of the Y123 film during heat treatment. The intensity ratio of the phonon O_d to O_a, $I(O_d)/I(O_a)$, is suitable to measure the volume fraction of the Y124 phase in a Y123-Y124 mixture, because the $I(O_d)$ is proportional to the number of atoms belonging to the double Cu-O chain and the A_g phonon of O_a around 500 cm^{-1} is common with the Y123 and Y124 phases.[13] For all heat treatments in 100 Torr O_2 between 600 and 800 °C, the value of $I(O_d)/I(O_a)$ remained (~ 0.91). This is the same as the value for as-prepared Y124 films and the Raman shifts of all A_g phonons also remained constant.

In order to test the thermal stability in reduced oxygen pressures, Y124 films were heated in 1 and 0.1 Torr oxygen at 600 °C, and 1 and 10 Torr at 700 °C. As is shown in Fig. 6, the Y124 film showed no changes in $I(O_d)/I(O_a)$ in 1 Torr at 600 °C, but changed drastically in 0.1 Torr O_2. At 700 °C the $I(O_d)/I(O_a)$ only slightly decreases $[I(O_d)/I(O_a)=0.84]$ in 10 Torr, while in 1 Torr O_2 the Y124 spectrum is absent. We have observed contributions from the $SrTiO_3$ substrate between 200 and 550 cm^{-1} (dotted curve), and from CuO, the peak at 295 cm^{-1}. The results of thermal treatment of the Y124 films are shown in a P_{O_2}-$1/T$ diagram of Fig. 7. Karipinski *et al.*[6] determined the stability ranges for Y123 and Y124 by means of annealing of 123 and CuO in high pressure O_2. They reported that the slope of the equilibrium line changes appreciably at $P_{O_2}=1$ bar (760 Torr) which they attributed to a change in the free energy of the reaction at high and low pressures. In Fig. 7 the broken line and dotted line correspond to the extrapolated equilibrium lines obtained from their experiments at $0.1 \leq P_{O_2} \leq 1$ bar and $1 \leq P_{O_2} \leq 3000$ bar, respectively. In the upper and right region of the equilibrium lines (lower T and higher P_{O_2}), the Y124 phase is more stable than the Y123 phase. The broken line is relatively close to the phase boundary reported by Lindemer *et al.*[9] Our results indicate their equilibrium line at lower pressure (broken line) is still applicable for the lower pressures usually encountered in thin-film processing.

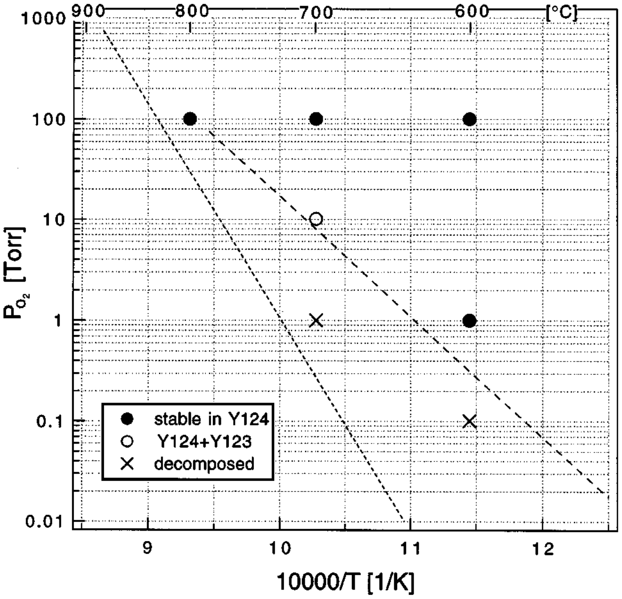

FIG. 7. The results of Y124 films through the heating treatments are mapped in a P_{O_2}-$1/T$ diagram. All films before heating were prepared as sample F_{450}. The broken line and dotted line correspond to the extrapolated equilibrium lines obtained by the experiments at $0.1 \leq P_{O_2} \leq 1$ bar and $1 \leq P_{O_2} \leq 3000$ bar, respectively (Ref. 6).

IV. CONCLUSION

Raman spectroscopy was performed to investigate the solid phase epitaxial growth of Y124 thin films. The films were synthesized through *in situ* annealing of precursors prepared between RT and 650 °C. The deposition temperature of the precursor was the most important parameter for the growth of Y124 films. For deposition temperatures above 500 °C the growth of Y124 was suppressed by the presence of Y211. Precursors deposited at 450 °C were transformed to optimum Y124 films by annealing at 750 °C in 100 Torr O_2 for 1 h. The thermal stability of Y124 films was examined by heat treatments for 1 h under $0.1 \leq P_{O_2} \leq 100$ Torr, $600 \leq T \leq 800$ °C. The films are stable up to 800 °C in 100 Torr O_2 and also at 600 °C in pressures as low as 1 Torr.

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