Phase intergrowth in Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ superconducting thin films prepared by single cylindrical-sputtering gun

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Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ thin films have been prepared in situ on MgO(100) by dc-sputtering employing a single cylindrical target. The thin films are of almost pure Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_8$ (2223) or intergrowth phases known as random stacking-fault structures of two phases having adjacent $n$. Deviations from the sputtering conditions for the 2223 growth induce the phase intergrowth of 2212, 2223, and 2234. The phase intergrowth occurs in connection with film compositions. © 1995 American Institute of Physics.

It is well known that there are several phases in the BiSrCaCuO system. The composition of each phase is expressed by a general formula of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$. Hereafter, we use the abbreviation 22($n$ - 1)$n$. In the series of 22($n$ - 1)$n$, 2223 is most attractive, because it has the highest superconducting transition temperature ($T_c$) of about 110 K. In spite of this potential of BiSrCaCuO, most applications of high-$T_c$ superconducting thin films are comparatively difficult. Single-phase Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ thin films with $n$ ≥ 3 have been prepared by artificial layer deposition methods, so-called layer-by-layer or block-by-block deposition, such as multitarget pulsed-laser-deposition (PLD) and multitarget sputtering or other methods, for instance, chemical vapor deposition of 2223 films. In comparison to multitarget sputtering, single-target sputtering is technologically more favorable. Nevertheless, there are only a few reports on the in situ growth of BiSrCaCuO thin films by single-target sputtering. Moreover, it is still unclear how the sputtering parameters influence the growth of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$.

In this letter, we report on the in situ thin film growth of 2223 by a single-target sputtering system. In the course of this study, we have observed that deviations from the sputtering conditions optimal for the 2223 growth induce phase intergrowth of 2212, 2223, and 2234, namely random stacking-fault structures of two phases having adjacent $n$. Intergrowth phenomena have been reported for 2212 films prepared by single-target PLD, but there seem to be no reports on the intergrowth in 2223 films except for artificially layered films.

We employed a dc-sputtering system equipped with a cylindrical sputtering gun, which is reliable in preparing YBaCuO thin films. In contrast to the sputtering gun described in Ref. 10, however, in this study we used it without a magnetic field, since magnetron sputtering creates a groove on the surface of the cylindrical target, which may cause a negative-ion bombardment problem. The cylindrical target of BiSrCaCuO had a composition of 2234. The total pressure ($P_{\text{total}}$) of the sputtering gas mixture (0.3 < $O_2$ / Ar < 2) ranged between 0.2 and 1.6 mbar. Above about 1.6 mbar, the sputtering was impracticable because of the instability of discharge and low deposition rates. Discharge power was varied between 60 and 160 W (250 – 330 V) in order to keep a deposition rate at about 1.5 nm/min. The thicknesses of the films ranged between 80 and 110 nm. The MgO(100) substrates were fixed to the heater block by silver paste and set in front of the gun at a distance of about 4 cm. The substrate temperature was varied between 700 and 800 °C, and controlled by using a resistive heater and a thermocouple placed inside the heater block and just below the substrate. After deposition the films were immediately cooled down to 600 °C within 3 min in the deposition atmosphere, and then kept for 10 min in 600-mbar $O_2$ at that temperature. Superconducting transitions were determined by four-probe resistive and inductive measurements. The films were analyzed by Rutherford backscattering spectroscopy (RBS) and x-ray diffraction (XRD) with Cu $K_{\alpha 1}$ radiation.

First, we investigated the dependence of the 2223 growth on $P_{\text{total}}$, keeping the $O_2$ / Ar mixture ratio constant at a value of one. The substrate temperatures were 10 – 20 °C lower than the melting point ($T_m$) of BiSrCaCuO, which depends on pressure. In this study, we determined $T_m$ as the temperature at which nonuniform films are obtained on the substrate. Figure 1 shows the typical change of the XRD patterns. In Fig. 1, all strong diffraction lines are assigned to Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_8$ (001) of the 2223 phase. Although a small amount of CuO impurity and an unknown phase having a peak at 2θ = 37.3° are present, there are no diffraction lines from other BiSrCaCuO phases such as 2201 and 2212, which have usually been observed in films prepared by postannealing. In the films shown in Fig. 1, the proportions of 2223 ($P_{2223}$) which will be discussed later are over 90%. The c-axis lattice parameters of these almost pure 2223 films are between 3.696 and 3.706 nm. The 2223 proportion of well-crystallized films reaches 100%, only when the substrate temperature is close to $T_m$ within a few degrees. Figure 2 shows the changes of the full width at half-maximum (FWHM) values of the (0010) diffraction lines and of rocking curves measured at the (0010) line. Both FWHM values decrease rapidly below 0.6 mbar and then gradually, as the $P_{\text{total}}$ increases. Evidently, the crystallinity and epitaxy are improved by increasing $P_{\text{total}}$. The above observations can...
be understood by the following explanations. As the oxygen partial pressure increases, $T_m$ of the 2223 films increases. The increase of $T_m$ allows us to deposit the films at higher temperatures. The deposition at a higher oxygen pressure and a higher temperature brings complete oxidation and swift migration of the sputtered species on the substrate, which may induce good crystallinity and epitaxy. Additionally, in dc-bias cylindrical sputtering of YBaCuO, it has been observed that $Ar^+$ ions accelerated by voltages above a threshold of 35 V create structural defects and degrade superconducting properties.\(^\text{12}\) This experiment suggests that $Ar^+$ ions scattered at the target surface may also show the same bombardment effects at low $P_{\text{total}}$. The bombardment effects can be reduced at high $P_{\text{total}}$ because of a short mean-free-path.

It has been demonstrated by the above-mentioned results that almost pure 2223 films can be prepared in a wide range of the sputtering parameters, i.e., at $P_{\text{total}}$ above 0.6 mbar and substrate temperatures between $T_m$ and about $T_m - 20^\circ\text{C}$, if the mixture ratio of $O_2/Ar$ is kept at about one. However, in order to obtain a narrow rocking curve of less than 0.2°, as observed for high $p_{2223}$ values, the substrate temperature is required to be very close to $T_m$ within a few degrees. The narrowest rocking curve of 0.15° was recorded in a film prepared at 760 °C, $P_{\text{total}}$ = 0.90 mbar, and $O_2/Ar$ = 0.8. That film showed partial melting at one edge of the sample. This is consistent with the established view that the heat treatment at a temperature as close as possible to $T_m$ is indispensable to obtain well-oriented BiSrCaCuO films.\(^\text{13}\)

Second, sputtering was performed on a variety of conditions, which are far afield from the 2223 growth. Typical XRD patterns are shown in Fig. 3 for the films deposited (a) at $P_{\text{total}}$ = 0.40 mbar, $O_2/Ar$ = 1.0, and 730 °C, (b) at $P_{\text{total}}$ = 0.60 mbar at 740 °C, (c) at $P_{\text{total}}$ = 0.80 mbar at 760 °C, and (d) at $P_{\text{total}}$ = 1.60 mbar at 775 °C. The substrate temperatures were 10–20 °C lower than the melting points. The 2223 proportions ($p_{2223}$) are also given in the figure.

![FIG. 1. XRD patterns of the films prepared at different sputtering gas pressure ($P_{\text{total}}$), keeping the $O_2/Ar$ ratio constant at one; (a) 0.40 mbar at 730 °C, (b) 0.60 mbar at 740 °C, (c) 0.80 mbar at 760 °C, and (d) 1.60 mbar at 775 °C. The substrate temperatures were 10–20 °C lower than the melting points. The 2223 proportions ($p_{2223}$) are also given in the figure.](image1)

![FIG. 2. FWHM values of the (0010) diffraction lines and of the rocking curves at that line as a function of $P_{\text{total}}$ for the films shown in Fig. 1. The best FWHM value of the rocking curves is 0.15°, which is not shown in the figure.](image2)

![FIG. 3. Continuous shift of the XRD patterns for the films prepared on the following conditions; (a) at $P_{\text{total}}$ = 0.80 mbar, $O_2/Ar$ = 1.0, and 730 °C, (b) at $P_{\text{total}}$ = 0.80 mbar, $O_2/Ar$ = 1.0, and 760 °C, (c) at $P_{\text{total}}$ = 0.70 mbar, $O_2/Ar$ = 1.3, and 760 °C, and (d) at $P_{\text{total}}$ = 0.20 mbar, $O_2/Ar$ = 1.0, and 730 °C. The intensities are normalized so that the heights of the strongest diffraction lines are the same.](image3)
well approximated by a linear relation of \( p = (\theta - \theta_{2212})/ (\theta_i - \theta_{2212}) \), where \( \theta \) is the Bragg angle and \( i \) is either 2201 or 2223.\(^6\) We apply this relation to the present films. In order to calculate the 2223 proportion \( p_{2223} \), the relative differences between the (0010) and (0012) diffraction lines for 2223 were used because of the variation of the c-axis lattice parameters, which causes an uncertainty in the calculation from the absolute position of (0010). The calculated \( p_{2223} \) values are indicated in Figs. 1 and 3.

It has been observed that the phase intergrowth is dependent on such sputtering parameters as the substrate temperature and the \( O_2/Ar \) ratio. Intergrowth phases of 2212 and 2223 are obtained by lowering the substrate temperature, as shown in Fig. 3 pattern (a), or by decreasing the \( O_2/Ar \) ratio from that optimal for the 2223 growth. On the other hand, the intergrowth of 2223 and 2234 in Fig. 3 pattern (c) occurs at the high \( O_2/Ar \) ratio. The observed intergrowth is consistent with the variation of the film compositions, as pointed out in Ref. 8. The compositions of the films were evaluated from the \( p_{2223} \) values and the RBS analyses. Figure 4 shows a comparison between these two sets of Cu/Bi ratios for all well-crystallized films. The data points exhibit an almost linear correlation between the XRD and RBS data. However, the slope of the data points deviates from the ideal line, which illustrates that excess Cu atoms probably forming CuO are present in the films. It can be noticed, therefore, that the excess Cu atoms are necessary for the phase intergrowth of 2223 and 2234.

In on-axis dc sputtering,\(^6\) it was pointed out that one of the causes of composition variation was resputtering due to negative oxygen ions. Contrarily, our cylindrical sputtering system is in principle off-axis, so that the resputtering can be neglected. In the present samples, it is plausible that thermally activated desorption is simply dominant for the composition variation. Bi\(_2\)O\(_3\) is expected to evaporate faster than the oxides for Sr, Ca, and Cu that are stable at our temperatures and \( O_2 \) pressures. At low substrate temperatures, therefore, a small re-evaporation rate of Bi results in the Bi-rich films and thus the grown phase is between 2212 and 2223. The idea of thermally activated desorption is also supported by a preliminary experiment of the deposition-rate dependence, which shows that films with high Cu/Bi ratios, namely intergrowth phases of 2223 and 2234, are obtained at lower deposition rates. In addition to the sputtering at low substrate temperatures, the films prepared at \( O_2/Ar \) ratios below one also have high Cu/Bi ratios. The influence of the Ar partial pressure may be explained by a change of the angular distribution of the sputtered species, which leads to the composition variation.

The superconducting properties of the almost pure 2223 films were poor. The films had \( T_c \) (onset) values in the resistive measurement of about 110 K, but zero resistance states were obtained at about 75 K. On the other hand, the extrapolations of \( R-T \) curves in the normal state nearly cross the horizontal axis at 0 K. Moreover, the films exhibited sharp transitions of about 2 K at about 75 K in the inductive measurement, which suggests that the films are spatially uniform. One of the causes of the broad transition may be a substitution between Ca and Sr, as reported for 2223 films prepared by MBE.\(^14\) In fact, the RBS data reveal a tendency of a lack of Sr and a surplus of Ca atoms, for example, Bi\(_{1.6}\)Sr\(_{1.7}\)Ca\(_{2.2}\)Cu\(_{3.0}\)O\(_{5+x}\) for a film having a \( T_c \) (zero) of 77 K. In addition, it has been pointed out that the superconducting transition is strongly influenced by the cooling process immediately after deposition,\(^15,16\) which means that the oxygen content must be optimized very carefully. This will be studied in future works.

In summary, we have prepared in situ thin films with almost pure 2223 phase by dc sputtering employing a single 2234 cylindrical target, the 2223 films can be obtained in a wide range of sputtering parameters. Deviations from the sputtering conditions for the 2223 growth induce phase intergrowth of 2212, 2223, and 2234. It has been observed that the intergrowth depends on the film composition.

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