In situ growth of epitaxial $Bi_2Sr_2CaCu_2O_{8-x}$ and $Bi_2Sr_2CuO_{6-x}$ films by pulsed laser ablation

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Pulsed-laser ablation has been used to grow epitaxial films of $Bi_2Sr_2CaCu_2O_{8-x}$ (Bi-2212) and $Bi_2Sr_2CuO_{6-x}$ (Bi-2201) on (001) MgO with entirely *in situ* processing. The films' layer-stacking sequence, microstructure, and superconducting T_c are highly sensitive to the growth temperature and deposition rate. Pure Bi-2212 films exist over only a narrow temperature range. Pure Bi-2201 films appear at higher growth temperature, while lower growth temperature enhances the Bi-2223 phase, though it is mixed with Bi-2212. The phase homogeneity, in-plane connections among grains, and superconducting T_c of Bi-2212 grown at a given temperature are greatly improved by reducing the deposition rate. Epitaxial Bi-2212 films grown at 740 °C and 0.5 Hz ($\sim$0.05 nm/s) have T_{c0} ($R=0$) = 71 K, with $J_c \sim 8\times10^5$ A/cm^2 at 50 K and $J_c \sim 5\times10^6$ A/cm^2 at 4.2 K.

Pulsed laser ablation (PLA) is widely used to grow epitaxial $YBa_2Cu_3O_{7-x}$ (YBCO) thin films, as well as multilayer and superlattice structures based on YBCO.[1,2] PLA has been used much less to grow epitaxial films in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (BSCCO) system, in part because several competing phases coexist, e.g., stable $n=1$, 2, 3 phases with zero-resistance $T_{c0} \sim 25$, 90, and 110 K, respectively, as well as metastable phases with higher n.[3,4] To obtain phase-purity, most epitaxial BSCCO films have been grown in two stages. The as-deposited films were annealed *in situ* or *ex situ* at different temperatures and oxygen pressures to enhance the growth of a particular phase.[5] Recently, however, several groups obtained as-grown epitaxial films of individual phases, though they used widely different growth conditions and methods. Instead of O_2, Kanai *et al.* used NO_2 and N_2O gases to obtain Bi-2201 thin films by PLA.[6] Bi-2212 epitaxial thin films have been formed with $T_{c0} \sim 80$ K using metalorganic chemical vapor deposition (MOCVD)[7,8] or by sputtering with multiple sources or off-stoichiometric targets.[9,10] A nearly pure Bi-2223 as-grown film was obtained by MOCVD with an extremely slow deposition rate, $\sim$1.2 nm per hour.[11] Although the T_c of as-grown PLA Bi-2212 epitaxial films was only $\sim$68 K,[5] they did have high J_c ($H=0$) $\sim 10^6$ A/cm^2 at $T=50$ K, which is almost one magnitude larger than some MOCVD films.[8]

These results suggest that BSCCO films are highly sensitive to growth conditions, including substrate temperature, oxygen pressure, incident atomic fluxes, and film-growth rate. Because PLA delivers atoms and ions to the growing film in a short-duration pulse, followed by a brief "annealing" period between pulses, it seems likely that BSCCO films grown by PLA would contain variations in stacking along the growth (c-axis) direction, as well as an increased defect density, both of which can affect superconducting properties. On the other hand, atoms and ions are delivered to the surface with both kinetic and internal (excitation) energy which may assist phase formation at low temperatures. Therefore, it is important to systematically study changes in phase-content, microstructure, and superconducting properties, as deposition conditions are varied, in order to improve the quality of PLA and other BSCCO films.

For PLA BSCCO films, the externally controlled growth conditions include the laser pulse repetition rate, laser energy density, substrate temperature, ambient oxidizer type, and pressure, and the target composition. In this letter, we examine BSCCO films grown using a polycrystalline stoichiometric Bi-2212 target and fixed oxygen pressure. X-ray diffraction (XRD) reveals that the major phase present in these films can be varied from $n=1$ to 3, in the homologous series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, as only the deposition rate and substrate temperature are changed. Moreover, films containing only the superconducting phases Bi-2212 or Bi-2201 (the latter accompanied by excess Ca and Cu from the Bi-2212 target) can be selected by careful control of these two variables. This striking phase selectivity is obtained simply by changing the PLA deposition conditions without changing the target composition.

Thin films were prepared by PLA on (001) single-crystal MgO substrates. The film c-axis was always perpendicular to the substrate. The details of the film growth instrumentation are reported elsewhere.[2] In brief, the KrF excimer laser beam with energy density $\sim$2 J/cm^2 and repetition rate from 0.5 to 3.3 Hz was directed at an angle of 45° onto a rotating stoichiometric Bi-2212 target. The PLA target was made from high-purity Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO powders. The substrates were mounted

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on the heater surface with silver paint, facing the target at a distance of 7 cm. Growth temperature was measured by a thermocouple embedded in the center of the heater block. Measurements using a second thermocouple indicated that the substrate surface temperature was about 50 °C lower than the heater block temperature (T_h). The ambient oxygen pressure during film deposition was 150 mTorr. Under these conditions, the film growth rate was ~0.1 nm/pulse. The sample thicknesses were ~400–600 nm as measured with a Dektak II profilometer. After deposition, the heater power was turned off and the films were cooled at an initial rate of 60 °C/min without changing the oxygen pressure. The films were taken out of the chamber at T_h~200 °C. Scanning tunneling microscope (STM) images were taken by a Nanoscope II STM in air; each sample was examined at several places. XRD patterns were obtained from a SCINTAG automated diffractometer equipped with Cu $K\alpha$ radiation (1.5418 Å) and a Ge detector. Thin film composition analysis was performed by energy dispersive analysis of x rays (EDAX) in conjunction with surface observation by scanning electron microscope (SEM).

Before considering our results, it is useful to know that Rubin *et al.*[12] have determined the phase-stability limits for bulk Bi-2212 and Bi-2223 specimens as a function of temperature and oxygen pressure using a solid-state electrochemical (coulometric titration) method. For both phases, they found a change of slope of the oxygen pressure versus temperature phase-stability boundary at 790–800 °C, indicating that both phases decompose by incongruent melting above this temperature but by solid-state reaction at lower temperatures. For Bi-2223, they found that (1) the solid-phase decomposition line coincides with the CuO-Cu_2O phase boundary and (2) the solid-phase decomposition is irreversible, consistent with the idea that Bi-2223 forms via solution-reprecipitation from a liquid phase. In contrast, the solid-phase decomposition of Bi-2212 (below ~790 °C) was found to be reversible. According to Rubin *et al.*, the phase stability boundary for Bi-2212 (Bi-2223) at our deposition pressure of 150 mTorr oxygen occurs at T~770 °C (~740 °C). Consequently, Bi-2212 grown under near-equilibrium conditions would be expected to be (barely) stable at T_h=800 °C (corresponding to substrate T~750 °C) but Bi-2223 would be unstable, decomposing into Bi-2212, Ca_2CuO_3, and Cu_2O.[12]

XRD of several films grown at 3.3 Hz deposition rate are shown in Fig. 1. The film grown at 800 °C [Fig. 1(c)] exhibits the Bi-2201 phase principally, with some minor unidentified XRD peaks. SEM/EDAX images reveal that the surface of this film is covered by a Cu-deficient (relative to the Bi-2212 target) granular-crystalline structure that is the Bi-2201 phase. Large particles scattered among the Bi-2201 grains are copper-rich unidentified phases. Thus, the Bi-2201 phase preferentially forms at high substrate temperature even though the target does not have the Bi-2201 stoichiometry. (Separate experiments using a polycrystalline, stoichiometric Bi-2201 target confirmed that single-phase epitaxial Bi-2201 films grow at 800 °C and 3.3 Hz.)[13] However, when the substrate temperature is

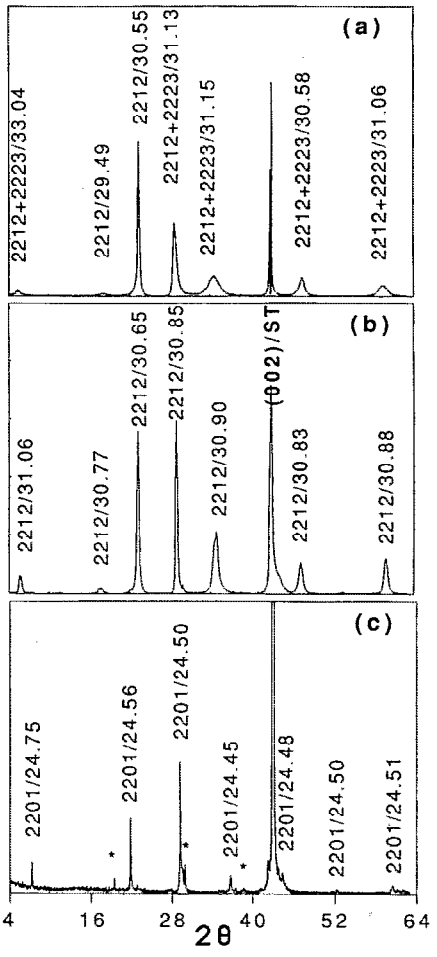

FIG. 1. X-ray diffraction patterns (Cu $K\alpha$ radiation) of films grown at 3.3 Hz and (a) 700 °C (2212 and 2223 phases), (b) 770 °C (2212 phase), and (c) 800 °C (2201 and 2212 phases), on (001) MgO substrates. The peak labeling is (phase/XRD lattice constant), with unidentified peaks denoted by *.

reduced, the Bi-2212 and Bi-2223 phases appear. An epitaxial thin film deposited at T_h=770 °C is essentially pure Bi-2212 [Fig. 1(b)], while the film grown at T_h=700 °C exhibits Bi-2223 as the major phase [Fig. 1(a)]. However, the broad x-ray peaks for the T_h=700 °C film suggest that it has mixed stacking of Bi-2223 and Bi-2212. A standard reference rocking curve through the (002) reflection of the MgO substrate had a full width at half-maximum (FWHM) value of 0.23°, whereas the rocking curve FWHM of the (0 0 20) reflection for the Bi-2212 film grown at T_h=770 °C was ~0.45°. The average length of the c-axis unit cell was 30.85 A for the T_h=770 °C (pure Bi-2212) film.

Combined STM and superconducting (zero-resistance) transition temperature, T_{c0}, measurements showed that the epitaxial film quality can be greatly improved by decreasing the deposition rate. A comparison of as-grown films at different growth temperatures and deposition rates is given in Table I. Interestingly, the BSCCO phase admixture changed only slightly, but T_{c0} improved markedly when the deposition rate was decreased from 3.3 to 0.5 Hz. A good pure Bi-2212 film, structurally similar to

TABLE I. Phase and T_c of films grown at different temperatures and deposition rates.

Rep. rate	0.5 Hz		3.3 Hz	
Temperature	Phase[a]	T_{c0} (K)	Phase[a]	T_{c0} (K)
800 °C	2201	···	2201+2212	···
770 °C	2212	68	2212	52
740 °C	2212	71	2212+2223	50
700 °C	2212+2223	35	2223+2212	15

[a]The major phase, determined by XRD, is underlined.

the film grown at T_h=770 °C and 3.3 Hz, formed at T_h =740 °C and 0.5 Hz. In contrast, the film grown at T_h =740 °C and 3.3 Hz contained some Bi-2223, apparently because the lower growth temperature and higher deposition rate permitted some of the Bi-2223 to be metastably "trapped" without converting to Bi-2212. Table I shows that for T_h<740 °C and with 150 mTorr oxygen pressure the films were a mixture of the Bi-2212 and Bi-2223 phases, apparently because atomic diffusion was not sufficient to avoid stacking disorder in the films. Because BSCCO is highly anisotropic, with large unit-cell dimensions along the layer-stacking direction, diffusion perpendicular to the layer structure is difficult. Subunits of the unit cell may attach to the growing film after each laser pulse and may easily create stacking faults. At a low deposition rate, these atoms can travel a greater distance between pulses and form the structure closer to the equilibrium stoichiometry, provided the growth temperature is not too low. The long growth time (~2 h for a 400 nm film at 0.5 Hz) also provides some low-pressure *in situ* annealing during film growth that may heal stacking faults and improve the Bi-2212 film structure. (However, we note that Schmitt, Schults, and Saemann-Ischenko[5] found that extended post-growth annealing of thin Bi-2212 films grown on $SrTiO_3$ degraded their superconducting properties, apparently because of a reaction between BSCCO and $SrTiO_3$.)

STM images of the in-plane crystalline structure of the predominantly or entirely Bi-2212 films grown at 740–770 °C support this description of the effect of deposition rate. The grains in the film grown at lower deposition rate were better aligned than in the film grown at higher deposition rate. The surface of the 740 °C, 0.5 Hz pure Bi-2212 film is also smoother than the others. The typical grain size was ~200 nm for the 740 °C films and ~500 nm for the 770 °C films. Within each grain, the films have a layerlike microstructure. The connections among grains of the low-deposition-rate films were good, while at the higher-deposition rate, the large grains were separated by deep gullies. This is believed to be the characteristic that directly affects the superconductivity of the films (Table I), due to weak links between grains.

Transport measurements of the resistance transitions are shown in Fig. 2 for the samples grown at 700, 740, and 770 °C with different deposition rates. The onset transition temperatures of the two Bi-2212 films were almost the same, 93 K, but T_c onset for the mixed-phase film was lower, with a similar trend in the T_{c0} values shown in Table I. The broad resistivity transitions of the 3.3 Hz films

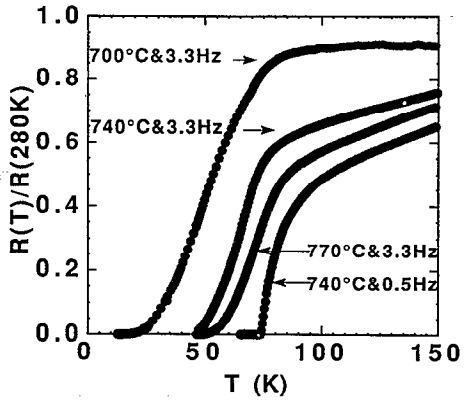

FIG. 2. Normalized (at T=280 K) resistivity vs temperature for films grown at different deposition rates and temperatures.

reveal inhomogeneity and weak links between grains, in agreement with the XRD and STM results. Although Bi-2223 occurs in the 700 and 740 °C 3.3 Hz films, their low onset T_c is probably due to stacking faults that lead to Josephson junctions between conducting layers. Similar behavior is revealed by the films' J_c values. Measured at zero magnetic field, the 740 °C, 0.5 Hz film had $J_c \sim 5\times10^6$ A/cm^2 at 4.2 K and $J_c \sim 8\times10^5$ A/cm^2 at 50 K, while the 740 °C, 3.3 Hz film had $J_c \sim 7\times10^5$ A/cm^2 at 4.2 K, an order of magnitude smaller.

In conclusion, as-grown films of pure Bi-2212 or Bi-2201 can be obtained by PLA with entirely *in situ* processing. However, the layer-stacking sequence, microstructure, and superconducting T_{c0} are highly sensitive growth temperature and deposition rate. Low deposition rate improves both the superconductive transition temperature and microstructure of PLA Bi-2212 films at a given growth temperature.

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