HIGH- T_c SUPERCONDUCTING $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ FILMS AND $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERLATTICES DEPOSITED BY LASER ABLATION

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High T_c superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}/\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superlattices with various periods and layer thicknesses were deposited by laser ablation on SrTiO_3 (100) single crystal substrates using an XeCl excimer laser ($\lambda = 308$ nm). The structure of the films was studied by SEM/EDS and X-ray diffraction. The films and superlattices deposited in an *in situ* process were epitaxial with the c-axis perpendicular to the substrate surface and the a- and b-axes parallel with the SrTiO_3 [100] or [010] directions. The electrical properties were studied by measuring the current-voltage characteristics, resistivity and critical current. For the *in situ* deposited $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films the zero resistivity temperature was 87 to 90 K and the critical current at 77 K was above 2×10^6 A/cm². For the films deposited at room temperature and post annealed under *in situ* deposition conditions, the critical temperature was the same, but the critical current was 0.5×10^6 A/cm².

INTRODUCTION

For the utilization of high T_c superconducting (HTS) materials in microelectronics, the material should be in the form of a film on a substrate, prepared by a physical or chemical deposition process. There are several requirements for the film and the process intended for applications:

The film should have

- high enough zero resistivity temperature T_c (the same as for corresponding bulk ceramic). This can be achieved by accurate stoichiometry (including oxygen content) and phase purity.
- high enough critical current j_c at operation temperatures (exceeding the bulk value by several orders of magnitude). The crucial factors are the choice of the superconducting compound, and the elimination of the effects of grain boundaries, which means highly oriented or epitaxial films. This in turn implies proper single crystal substrate material.
- low surface resistance (for microwave applications)
- homogeneous single-phase structure
- smooth surface

In addition, the deposition process should make it possible to grow layered structures of superconductors and other materials (insulators, normal conductors, etc.) with high accuracy in thickness.

Most of these requirements are fulfilled by the laser ablation deposition process, which is equal to or better than any other method, the only exception being the surface smoothness. Laser ablation deposition is especially suitable for multicomponent systems and for superlattices because of the reproducibility of stoichiometry and the easy control of the thickness of layers.

In the first laser ablation deposition experiments of HTS materials¹, the deposition was performed at low temperatures and the films were post annealed in conditions resembling those of sintering of the bulk materials. The highest quality high T_c superconducting 1-2-3 type films², as well as superlattices consisting of layers of different 1-2-3 type materials³⁻⁶, have been produced by an *in situ* growth process. Low-temperature deposition processes utilizing post-annealing at relatively low temperatures and low oxygen partial pressures have also been developed⁷.

High T_c superconductors are naturally layered structures where the Cu-O planes as well as the interaction between them plays an important role. Therefore, it is interesting to study the possibility of growing artificially layered structures, where the thickness of the superconducting layers, as well as the thickness of the separating material, can be varied on a unit cell scale. On the other hand, for superconductive device applications, it is important to develop techniques for fabricating planar superconductor/non-superconducting structures on a nanometer scale due to the small coherence length of high T_c superconductors.

Recently, it has become possible to grow short period superlattices of different $REBa_2Cu_3O_{7-d}$ 1-2-3-type superconductors either by sputtering^{3,5} or laser ablation deposition^{4,6}. The rare earth (*RE*) atoms involved in the structures have been Y, Dy, and Pr. In $YBa_2Cu_3O_{7-δ}/PrBa_2Cu_3O_{7-δ}$ (YBCO/PrBCO) superlattices, superconducting YBCO layers are separated by non-superconducting PrBCO layers. PrBCO is a semiconductor-like 1-2-3-compound with high resistivity at low temperatures. It has the same crystal structure as YBCO and has a good lattice match with it. Because epitaxial films of these materials can be grown under similar conditions, the deposition of superlattices by laser ablation is quite straightforward. In this study, YBCO/PrBCO superlattice films were deposited on $SrTiO_3$ substrates by an *in situ* process, which is necessary for high quality epitaxial growth, as well as for obtaining sharp layer interfaces. The properties of the superlattices were then compared to those of epitaxial YBCO and $Y_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-δ}$ films.

EXPERIMENTAL

Deposition Process

YBCO and PrBCO films, YBCO/PrBCO superlattices and $Y_{0.5}Pr_{0.5}Ba_2Cu_3O_{7-δ}$ films were deposited on heated (700–750°C) $SrTiO_3$ (100) single crystal substrates using an XeCl excimer laser ($\lambda = 308$ nm, 40 mJ/pulse, energy density 2–3 J/cm², repetition rate 25–50 Hz) and oxygen flow (0.25 mbar O_2) during the deposition. The laser beam was scanned over a sintered ceramic target held at an angle of 45 degrees to the laser beam. The target-to-substrate distance was 3 cm. The ablation process was carried out in a vacuum chamber with a base pressure of about 10^{-5}

mbar. After the deposition, the temperature was lowered to 450°C while the oxygen pressure was increased to 500 mbar. The films were kept at 450°C for 10 min to assure maximum oxygen intake. For the deposition of superlattices, the laser beam was scanned over two targets placed closely together. It was possible to control the thickness of each layer independently by varying the number of pulses. Typical deposition rates were about 0.1 Å/pulse (2.5–5 Å/s). For comparison, YBCO films were deposited on non-heated substrates and post annealed for 1 h under the above-mentioned *in situ* deposition conditions.

Film Characterisation

The films were characterised by X-ray diffraction and electrical measurements. The electrical measurements were carried out using the standard four-point probe method. The electrical contacts were attached to the surface of the films using silver paint. The resistivity curves were measured using current densities of about 1 A/cm². For the measurement of current-voltage characteristics and critical currents, the films were patterned by using a focused beam from a Nd:YAG laser ($\lambda = 532$ nm). Typical pattern widths were 30 μm for the YBCO films and 80 μm for the superlattices.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

The x-ray diffraction patterns of YBCO and PrBCO thin films and YBCO/PrBCO superlattices on SrTiO₃ (Fig. 1) displayed only strong (00l) type reflections showing perfect c-axis orientation. The in-plane epitaxy of the *in situ* deposited films and superlattices was confirmed, as in our previous study⁶, by a ϕ -scan of the (104) and (014) reflections from a tilted sample where only sharp reflections 90° apart were seen. This indicated that the films were epitaxial with the c-axis perpendicular to the SrTiO₃ (001) surface plane and the a- and b-axes parallel (within 1°) with the SrTiO₃ [100] or [010] directions. For the post-annealed YBCO films, the in-plane epitaxy was poorer.

The periodicity of the superlattices was studied by observing satellite lines in the diffraction pattern. For a superlattice with a period of n unit cells in the direction of c-axis, satellite peaks occur at positions $(0, 0, l \pm 1/n)$ in the direction [001] of the reciprocal lattice. Fig. 2 shows the satellite lines near the (001) and (002) reflections, corresponding to the periods of (a) 26 nm ($11 + 11$ unit cells) and (b) 4.8 nm ($2 + 2$ unit cells). Superlattice lines were observed even for non-integer number of unit cells; in that case, the interfacial layers contained both YBCO and PrBCO unit cells.

Electrical Properties

The zero resistivity temperature, T_{c0} , of the *in situ* deposited epitaxial YBCO films was 87–90 K and the $R(T)$ curve, Fig. 3(a), extrapolated well to zero, yielding the

FIGURE 1 X-ray diffraction patterns (CuK α) of *in situ* deposited films: (a) YBa₂Cu₃O_{7- δ} , (b) YBa₂Cu₃O_{7- δ} /PrBa₂Cu₃O_{7- δ} superlattice, period 4.8 nm (2 + 2 unit cells), (c) PrBa₂Cu₃O_{7- δ} .

resistance ratio $R(300)/R(100)$ near 3 and resistivity $\rho(100\text{ K}) \approx 60\ \mu\Omega\text{cm}$. All these properties are common for good quality epitaxial films. For the post-annealed films (Fig. 3(b)), the resistance ratio was about the same but the resistivity $\rho(100\text{ K})$ was somewhat higher. T_{c0} was in the same range as for the *in situ* deposited film and for the target material (Fig. 3(c)). Fig 3(d) displays the semiconductor-like behavior of an *in situ* deposited PrBCO film.

The temperature dependence of resistivity for the 2/2 and 1/1 unit cell period superlattices are presented in Figure 4(a) and (b). The respective critical temperatures, 57 and 31 K, are lower than for YBCO but considerably higher than for the alloy Y_{0.5}Pr_{0.5}Ba₂Cu₃O_{7- δ} (18 K, Figure 4c). For longer period superlattices, the resistivity curves and critical temperatures approach those of YBCO films. All superlattice films showed metallic behavior above T_c but the resistivity ratio was considerably less than 3.

The 1/1 unit cell 'superlattice' did not show satellite lines in the X-ray diffraction pattern. However, its resistivity curve had a positive slope contrary to the Y_{0.5}Pr_{0.5}Ba₂Cu₃O_{7- δ} material, and its T_{c0} was at least 12 K higher so that Y and Pr were not randomly distributed in the rare earth sites. Recent scanning tunneling microscopy⁸ and high resolution electron microscopy⁹ studies of the nucleation and growth of epitaxial YBCO films and superlattices suggest terraced unit cell by unit

FIGURE 2 X-ray diffraction patterns ($\text{CuK}\alpha$) of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}/\text{PrBa}_2\text{Cu}_3\text{O}_{7.8}$ superlattices in the region of (001) and (002) reflections, showing satellite lines (arrows): (a) period 26 nm (11 + 11 unit cells), thickness 270 nm; (b) period 4.8 nm (2 + 2 unit cells), thickness 97 nm (schematic structure in inset).

cell growth. The growth occurs along the edges of two-dimensional island nuclei that are one or two unit cells high, so that in a layer of a 1/1 unit cell superlattice there may be regions of 0, 1 and 2 unit cells in thickness; this may explain the lack of satellite lines in the 1/1 'superlattice'.

The critical current measured from laser-patterned films (width of lines 10–30 μm) in a zero applied magnetic field at 77 K were in the range $1\text{--}2.5 \times 10^6 \text{ A/cm}^2$ for the *in situ* deposited YBCO films and $0.2\text{--}0.5 \times 10^6 \text{ A/cm}^2$ for the post-annealed films. For a 4/4 superlattice stripe with $T_{c0} = 42 \text{ K}$, the critical currents at 30 K and 15 K were $0.2 \times 10^6 \text{ A/cm}^2$ and $2.6 \times 10^6 \text{ A/cm}^2$, respectively.

FIGURE 3 Relative resistance $R(T)/R(300\text{ K})$ of films on SrTiO_3 : (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ deposited by an *in situ* process and (b) at room temperature and post annealed, (c) $\text{PrBa}_2\text{Cu}_3\text{O}_{7.8}$ deposited by an *in situ* process (d) $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ target material.

CONCLUSIONS

Laser ablation deposition is especially suitable for multicomponent systems and for superlattices because of stoichiometric reproducibility and the ease with which layer thickness can be adjusted.

YBCO films and YBCO/PrBCO superlattices with good epitaxy were grown on SrTiO_3 by an *in situ* laser ablation process. Room temperature deposition of YBCO films yielded equally high critical temperature but poorer epitaxy and somewhat lower critical current. All superlattices showed metallic resistivity behavior above T_c . The zero resistivity temperature of the superlattices decreased when the period

FIGURE 4 Relative resistance $R(T)/R(300\text{ K})$ of films on SrTiO_3 : (a) (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}/\text{PrBa}_2\text{Cu}_3\text{O}_{7.8}$ superlattice, period 4.8 nm (2 + 2 unit cells), thickness 97 nm (21 + 20 layers). (b) period 2.4 nm (1 + 1 unit cells), thickness 58 nm (25 + 24 layers), (c) alloy $\text{Y}_{0.5}\text{Pr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$.

(and the superconducting layer thickness) decreased. The shortest period in superlattices showing clear satellite lines in X-ray diffraction was 2/2 unit cells (4.8 nm), but even the 1/1 unit cell film had some properties of a layered structure, so that the deposition technique is just at the limit of 1 unit cell (≈ 1 nm) accuracy. The ability of depositing very thin epitaxial superconducting, non-superconducting and insulating layers with high accuracy is also important in device applications.

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