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Reactive rapid sequential pulse laser deposition of $YBa_2Cu_3O_7$: A candidate to eliminate particulate formation

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We propose a modified version of pulsed laser deposition: rapid sequential pulsed laser deposition. In this method, different metal elements are sequentially deposited onto a substrate in a fixed stoichiometric ratio in a very short period of time. This method allows a flexible choice of target material and of laser power density, which may solve the particulate problem intrinsic to a conventional laser ablation. We show results of an *in situ* formation of $YBa_2Cu_3O_7$ thin film as a demonstration of this method.

Pulsed laser deposition (PLD) is regarded as a powerful method to form ceramic thin films. For example, high-T_c superconducting films with excellent electrical properties such as a high-T_c and J_c, low microwave surface resistance, and good crystallinity as measured by narrow rocking curve widths have been reported.[1] Despite a local flatness and a layer-by-layer growth as observed by reflection high-energy electron diffraction (RHEED) oscillations,[2,3] a serious problem in PLD remains to be solved: particulate or boulder formation. Careful studies of high-T_c films have led to classification of particles into two groups:[4,5] precipitates, which are also observed in films formed by the other methods, and particulates, which are unique to films grown by PLD.

A general solution to eliminate particulates has not yet been found. However, two methods to reduce the particulates on the film surface have been reported to be effective: (1) use of velocity filters,[6] (2) an off-axis PLD.[7] The latter method is useful under condition of high ambient pressure.

There are also other problems in a conventional PLD. Although relatively simple control of the film composition is one of the primary merits of the PLD technique, it is achieved only within a narrow range of gas pressure, target-substrate distance (T/S), and laser power density. Furthermore, the composition of the target surface is found to change over time with increasing amount of laser irradiations.[8]

We have observed that particulate density per thickness was reduced by two methods: (1) lowering laser power density, (2) using a target with a simple composition such as metals. Based on these observations, we have pursued a solution of the above problems. However, reduction of laser power density degraded the stoichiometry of film.[9] As a result, this increases precipitates at substrate temperature (T_s) suitable to obtain good electrical properties. One may solve this by using a nonstoichiometric target but this usually worsens the particulate problem, or one may reduce T_s and suppress precipitates by sacrificing electrical properties. Instead, we use several targets and sequentially irradiate them.

A sequential deposition may cause other problems such as the *formation of the secondary phase* due to a local nonstoichiometric composition (Fig. 1) as discussed by Kanai *et al.*[2] in the layer-by-layer deposition of the cuprates. To avoid this problem, an average composition at the film surface is controlled to have correct stoichiometry within a very short time. To accomplish this, laser power density needs to be suitably adjusted for each target, because of a critical dependence of evaporation rate on a target material. Due to the above argument, this adjustment should be very responsive.

We call this version of PLD rapid sequential PLD (RS-PLD). RS-PLD can offer a flexible choice of target material and T/S, as well as free choice of the gas pressure and the excitation of the evaporated elements which are given by conventional PLD.

A RS-PLD system was assembled to meet the above requirements. The ArF laser is triggered as selected portions of selected targets are moved into the laser beam. The attenuator controls the laser power suitable to each target within 1 ms. Stoichiometry of a film is controlled by power density and the number of the laser pulses on each target per cycle. In the case of $YBa_2Cu_3O_7$ film, Y, Ba, and Cu atoms with a molar ration of 1:2:3 are deposited onto the substrate in one cycle of 100–200 ms.

$YBa_2Cu_3O_7$ (YBCO) films grown by PLD exhibit a higher than average number of particulates compared to

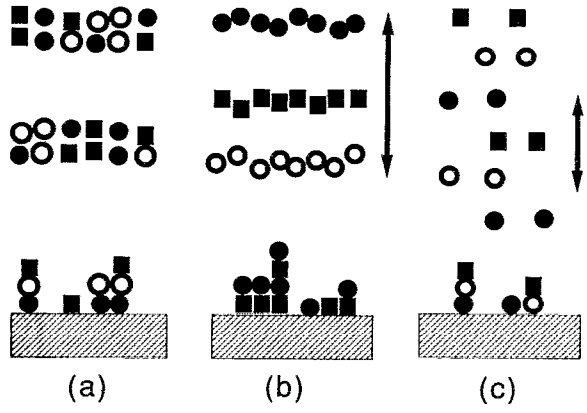

FIG. 1. Schematic diagram showing deposition process of an oxide $ABCO_x$ by three methods: (a) conventional PLD, (b) layer-by-layer deposition, (c) RS-PLD. Metal elements A, B, and C are denoted by (●), (○), and (□), respectively. The arrows show timescales of one cycle which are typically 1 min in (b) and 0.1 s in (c). $ABCO_x$ film has a crystal structure of ABCAB-CABC. This can grow at given temperature and pressure with correct stoichiometry. If a certain element, e.g., B is absent for awhile, secondary phase AC can grow as shown in (b).

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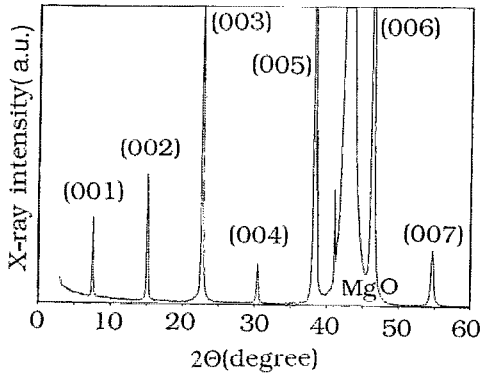

FIG. 2. $\theta/2\theta$ x-ray diffractometer pattern of 500 Å thick YBCO films on a MgO (100) substrate.

films of other oxide materials. Therefore, we have used RS-PLD to deposit this material in order to test its efficiency. Within our knowledge, this is also the first report of a PLD growth of YBCO using metal targets, of a sequential PLD deposition of YBCO, and of the growth of YBCO with T_c=90 K by all kinds of *in situ* sequential depositions.

For deposition of YBCO, it would be ideal if we could use Cu, Ba, and Y as targets. However, the evaporation rate of Cu for power density of a few Joule cm^{-2} was extremely low. Therefore, we used Ba and YCu_3 after carefully examining deposition rate and morphology of films deposited at room temperature using many targets.[9]

Homogeneous YBCO was deposited onto 1 cm^2 $SrTiO_3$ (100) and MgO (100) substrates. Typical energy densities were about 0.2 J/cm^2 for Ba targets and about 1.5 J/cm^2 for YCu_3. The average deposition rate was about 0.005 A/pulse or about 7 A/min. A substrate was set at a distance of 80 mm from targets, and T_s was between 600 and 650 °C. Molecular oxygen pressure in the chamber was between 50 and 100 mTorr.

Figure 2 shows the $\theta/2\theta$ x-ray diffractometer pattern of a YBCO thin film on a MgO (100) substrate. The dominant (00ℓ) peaks indicate that the sample was c-axis oriented with the [001] direction perpendicular to the film surface. The c-axis lattice constants calculated from the (00ℓ) peaks of these samples agreed with the bulk-value within 0.3%. This suggests that the films were well-oxidized despite the use of metal targets.

Surface morphology was studied with an optical microscope and a scanning electron microscope (SEM). The average compositions of the films were analyzed by x-ray fluorescent spectroscopy and inductively coupled plasma spectroscopy, and local compositional variation was studied by a SEM equipped with EDX. Particles were found on film surface which did not have an exact stoichiometry. In these films, impurity phases were detected by x-ray diffraction. However, these particles had very irregular shapes and compositions different from the matrix. They were drastically reduced in number and size, when the films had a correct stoichiometry or were deposited at a lower T_s. Therefore, we concluded that these particles were precipitates as discussed in the literature.[4,5] No particles larger than a half micron

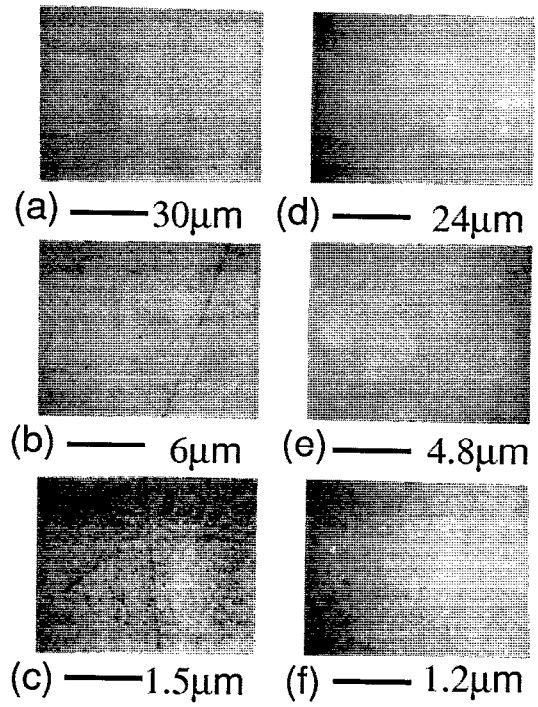

FIG. 3. SEM pictures of 500 Å thick YBCO films on a $SrTiO_3$ (100) substrate (a), (b), (c) and a MgO (100) substrate at different magnifications (d), (e), (f).

were observed on the entire surface of the films as long as the film had an exact stoichiometry.

Figures 3(a) and 3(c) show the SEM pictures of a YBCO film on a $SrTiO_3$ with a good stoichiometry. Figures 3(d), 3(e), and 3(f) show those of the same film on a MgO substrate. The film on the $SrTiO_3$ had zero resistance at 80 K as shown in Fig. 4 and a thickness of approximately 500 Å, whereas the film on the MgO showed zero resistance at 77 K. The bright spots in the low magnification pictures were confirmed to be precipitates or grain boundaries. The pictures at different magnifications clearly demonstrate that no particulates were observed, and that only a few precipitates smaller than 0.1 μm were observed in the area of 100 μm by 100 μm. There were no particulates identified by shape and size (>a half micron in diameter) in 1 mm×1 mm area of the

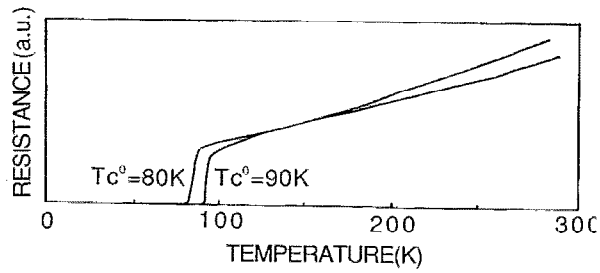

FIG. 4. Temperature dependence of resistance of YBCO film stripes on $SrTiO_3$ (100). The sample with T_c=80 K has resistivity of 400 $\mu\Omega$ cm at 300 K, and the sample with T_c=90 K has resistivity of 200 $\mu\Omega$ at 300 K.

film surface even after the targets were used for more than 10 runs. Hence, we believe we could substantially eliminate particulate formation inherent to PLD.

The YBCO film on Figs. 3(a)–3(c) was cut into a 2 mm×8 mm stripe and the temperature dependence of the critical current density J_c was measured by a standard 4 probe method. Contacts were formed with silver paste and the distance between voltage probes was 4 mm. J_c of the film was 5×10^5 A cm^{-2} at 70 K. Another 500 Å thick film on $SrTiO_3$ showed zero resistance at 90 K as in Fig. 4. This film had the J_c of 5×10^5 A cm^{-2} at 77 K. However, precipitates were easily found on the film surface, though it had few particulates. This film was Ba poor and the precipitates were confirmed to be CuO.

It would be interesting to compare the present method with other similar approaches. An atomic layer-by-layer deposition is a variation of the sequential deposition method. The elimination of particulates by this version of PLD has not yet been reported. Moreover, problems associated with a layer-by-layer deposition have been discussed by several groups.[2,10] Tukamoto *et al.* have reported that $HoBa_2Cu_3O_7$ was not obtained due to formation of secondary phases when it was deposited layer-by-layer via a reactive evaporation.[10] The critical temperatures of YBCO-type superconductors grown layer-by-layer via MBE and sputtering have been much lower than the bulk value.[11–13]

In addition to the elimination of particulates, the alleviation of a strict ablation threshold to maintain stoichiometry of a multicompositional target onto the film, offers other advantages. RS-PLD can use a very low power laser such as laser diodes by using proper target materials. *Metal halides* are one of the suitable targets for this purpose. They were found to evaporate by laser power density 1–2 orders lower than that used for metal oxides, and to oxidize easily in an oxygen environment at elevated temperature, e.g., >500 °C.[9]

In conclusion, we have proposed a new version of PLD which can substantially eliminate particulate formation as shown by the results on an *in situ* formation of $YBa_2Cu_3O_7$ films typically with T_c of 80 K. The present investigation shows that $YBa_2Cu_3O_7$ can be formed by a sequential deposition using PLD, also that $YBa_2Cu_3O_7$ can be made by a reactive PLD using metal targets, and that the resulting material can have T_c of up to 90 K. Additionally, we discussed the possibility of a PLD with a very low power laser.

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