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Microstructures and enhancement of critical current density in YBa/sub 2/Cu/sub 3/O/sub 7/ thin films grown by pulsed laser deposition on various single crystal substrates modified by Ag nano-dots

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Microstructures and Enhancement of Critical Current Density in $YBa_2Cu_3O_7$ Thin Films Grown by Pulsed Laser Deposition on Various Single Crystal Substrates Modified by Ag Nano-Dots

A. H. Li, M. Ionescu, H. K. Liu, T. Silver, X. L. Wang, and S. X. Dou

***Abstract*—$YBa_2Cu_3O_7$ (Y123) thin films were grown by pulsed laser deposition (PLD) on YSZ (100), SrTiO3 (100), and LaAlO3 (100) single crystal substrates. Prior to the film deposition, a discontinuous layer of Ag nano-dots was deposited on the substrates. The Y123 films grown on such surfaces modified with Ag nano-dots were characterized by Atomic Force Microscopy (AFM), X-ray diffraction (XRD), scanning electron microscopy (SEM), AC susceptibility and DC magnetization. The effects of the density of Ag nano-dots, which was controlled by the numbers of PLD shots, on the microstructures and resultant critical current density J_c have been studied systematically. Results showed that at fixed physical deposition conditions J_c increased monotonically with number of Ag shots, n, for films grown on both STO and LAO substrates. At 77 K, the J_c increased from 10^6 to 3.2×10^6 A/cm^2 for LAO and from 8×10^5 to 3.5×106 A/cm^2 for STO as n increased from 0 to 150. At 5 K, the enhancement of J_c was approximately four times at both low and high fields. However, for films grown on YSZ substrate, J_c increased from 2×10^5 to 2×10^6 A/cm^2 as Ag shots increased from 0 to 30, and decreased to 9×10^5 for $n \geq 60$. Detailed microstructure investigations indicated that the crystallinity and *ab* alignment gradually improved as the number of Ag-nano-dots increased.**

***Index Terms*—Critical current density, laser deposition, microstructures, nano-doping, substrate, superconducting films.**

I. Introduction

DUE TO potential significant applications for superconducting coated conductors based on $YBa_2Cu_3O_y$ (Y123) thin film technology, extensive studies are currently being carried out worldwide on Y123 films grown on different single crystal or metal based substrates. For applications of Y123 thin films and coated conductors at 77 K, high values of J_c are required. This requirement has stimulated extensive exploration of various means of introducing effective pinning centers into Y123.

Incorporation of nano-size oxide particles [2], [3] or metal particles [4], [5] has proved to be an alternative economic approach to enhance critical current density J_c in either low or high magnetic fields for Y123. Y123 films with nano-Ag particle inclusions exhibited higher J_c values compared to pure Y123 films. It has been reported that, by creating an array of Ag or CeO_2 or Y_2O_3 [6], [7] nano-dots in-situ on the substrates prior to the deposition of superconducting films, the J_c was greatly enhanced for $(Tl, Cu)BaSrCa_2Cu_3O_y$ (TBCO) and Y123 thin films [4], [5]. The nano-dots could introduce extended defects into the TBCO and Y123 films resulting in strong pinning centers if they were deposited on the substrate prior to the deposition of the films. However, it is still not clear how the metallic Ag nano-dots play a role in the improvement of J_c in Y123 films with nano-inclusions. In this paper, we introduced the Ag nano-dots onto the surfaces of different single crystal substrates, STO, YSZ and LAO, or the substrate surfaces were modified by Ag nano-dots, prior to the deposition of Y123 films. The effect of the amount of nano-Ag dots on the film performance has been systematically investigated. We found that, under fixed physical deposition conditions, such as oxygen pressure, substrate temperature, etc., the J_c of Y123 films deposited on such surface modified substrates is greatly enhanced with much improved c-axis alignment in comparison to the films grown on substrates without Ag nano-dot modification. The underlying mechanisms relating to the improvement of microstructures under the influence of Ag-nano-dots are presented.

II. Experimental

The degree of lattice mismatch between Y123 and substrates controls the alignment of Y123 grains. In order to see how the Ag-nano-dots play a role in Y123 performance when grown on substrates with different degrees of lattice mismatch, we chose to use three different single crystal substrates, YSZ, $LaAlO_3$ and $SrTiO_3$. YSZ has a poor lattice match with Y123 compared to LAO and STO.

The fabrication of the nano-Ag dots and Y123 films used in this study was carried out using a standard PLD system, comprising a deposition chamber with a base pressure of 10^{-7} Torr, fitted with a resistive sample heater, and a 6 target manipulator. A KrF excimer laser, with a wavelength of 248 nm was used as the ablating power source. The laser beam was focused onto the rotating target by a fixed-beam optical train.

Prior to the deposition of Y123 films, a thin layer of Ag nano-dots was PLD deposited on the 3×3 mm^2 YSZ, LAO and STO substrates by ablating a pure Ag target at 780°C and

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the base pressure of the deposition chamber, using a laser energy of 300 mJ/pulse. Samples of Y123 films (with 0, 15, 30, 60, 150 Ag shots) used in this study were grown on YSZ, LAO and STO substrates whose surfaces were modified by different amounts of Ag nano-dots that were controlled by the number of shots ablated from the Ag target. The Y123 thin films were also grown by PLD, which was carried out at 780°C, at a pressure of 400 mTorr of high purity oxygen, using a laser repetition rate of 6 Hz, and a laser energy of 300 mJ/pulse. After the deposition, the Y123 film was annealed for one hour at 550°C at a pressure of 760 Torr of oxygen, followed by a slow cooling to 400°C in 30 min, where the films were held for 10 min and then free cooled to room temperature. The Y123 films produced were approximately 400 nm thick. The surface morphologies of the Ag dots on the substrates and the Y123 films grown on the different substrates were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Y123 phase formation was assessed by X-ray diffraction (XRD). The superconducting transition temperature, T_c for all films was measured by AC susceptibility, and the critical current density, J_c for all films was estimated from DC magnetization hysteresis loops measured over a wide temperature range at 5, 10, 20, 30, 40, 50, 60, 70, and 77 K in external DC fields of up to 5 T parallel to the c-axis of the films using a commercial magnetic property measurement system.

III. Results and Discussions

The shape and distribution of the Ag nano-dots deposited on YSZ substrate were investigated by AFM. The results showed that for different Ag shots, Ag formed as nano-dots on the substrate surfaces. The average density of these dots is approximately 2–10/μm^2, which increases as the number of Ag shots increases. The height of the Ag dots is between 0.2 nm and 2 nm with a diameter of 10–20 nm. It was also found that the Ag nano-dots tended to grow together and formed islands on the surfaces of the YSZ substrate when the number of Ag shots, n, was greater than 30. These islands were found to have diameters of 100 nm and consisted of 10–20 individual Ag dots.

The J_c was calculated from magnetic hysteresis loops measured at different temperatures using the Bean model, $J_c = 20\Delta M/[a(1 - a/3b)]$, where a and b are the sample dimensions, with a< b. The field dependence of J_c at 5 K is shown in Fig. 1. It can be clearly seen that the J_c increases as the Ag shots increase from 0 to 30, at both low and high field. J_c then drops slightly for $n = 60$ and remains constant until $n = 150$. The field dependence of J_c vs the number of Ag shots at 0 and 77 K exhibited quite similar trends.

The Ag shot dependence of J_c measured at 5, 40 and 77 K in zero field and 1 T (77 K) and 5 T was plotted in Fig. 2. It can be seen that for all the measured temperatures, the zero field J_c increased monotonically as the number of Ag shots n increased from 0 up to 30, dropped slightly for $n = 60$, then remained constant for all the measured temperatures of 5, 40 and 77 K. The same trend is also seen for the J_c at 5 K and 4 T, however, for 40 K and 4 T, J_c reached a maximum for Ag shots $n = 15$, then dropped as $n > 15$. Furthermore, the J_c at 77 K and 1 T increased with the number of Ag shots n up to 150 in contrast with

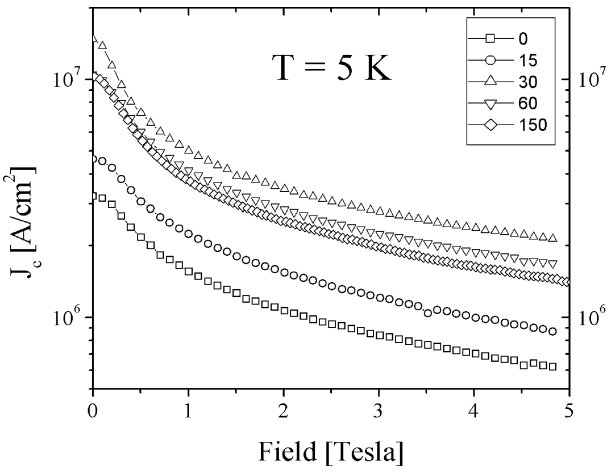

Fig. 1. Field dependence of J_c at 5 K for Y123 films grown on YSZ (100) with different numbers of Ag shots.

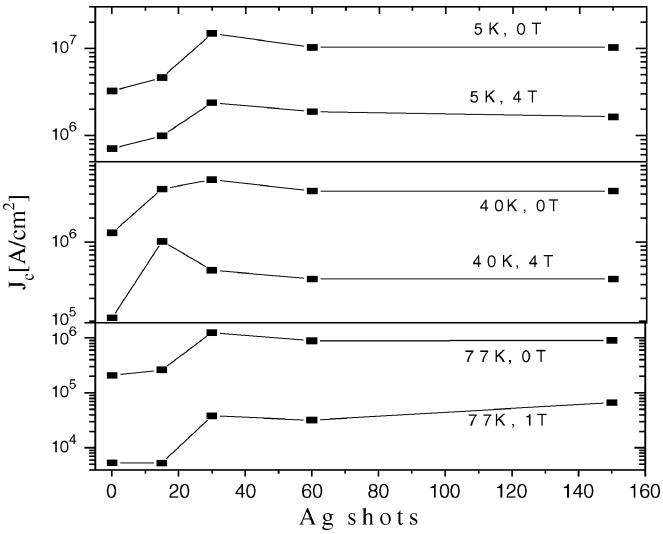

Fig. 2. The Ag shot dependence of J_c for Y123 film grown on YSZ (100).

all other J_c values. These results show that for Y123 film grown on YSZ the introduction of Ag-nano-dots onto the substrates prior to the deposition of Y123 thin films really played a role in enhancing the J_c at both low field and high field. There seems to be an optimum number of Ag shots producing optimum J_c. This trend relating to the number of Ag shots for our Y123 film grown on YSZ is agreement with what has been observed in Y123/STO films that were made from a target of Y123 mixed with Ag particles [4]. At 77 K, the J_c increases from 2×10^5 up to 1.2×10^6 A/cm^2, when the number of Ag shots increased from 0 to 15. We have to point out that although the physical deposition is not optimized (as the reference sample J_c is low) all the deposition conditions were fixed for all the film depositions so that the only difference is in the number of Ag shots.

It should be emphasized that all the Y123 films were laserdeposited under the same ablation conditions, such as the same oxygen pressure, substrate temperature, laser energy, etc. The only difference is the amount of Ag dots deposited on the substrates prior to the deposition the Y123 films. It worth pointing out that the J_c values at 77 and 5 K for the reference sample (with zero Ag shots) are relatively low compared to pure Y123

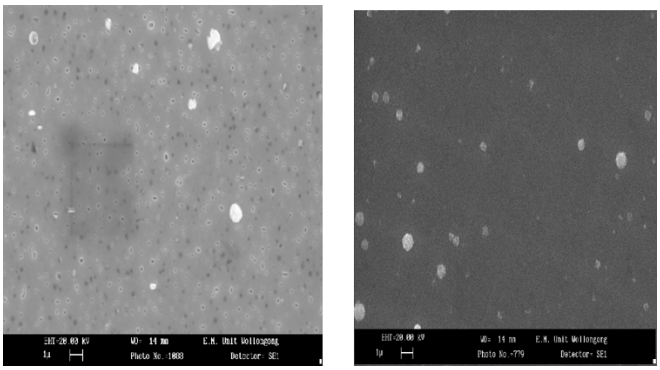

Fig. 3. SEM image for Y123 film grown on YSZ with 30 (right) and 150 (left) shots of Ag.

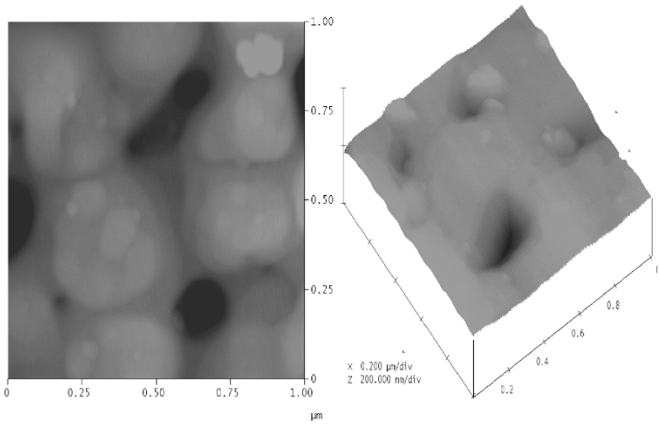

Fig. 4. AFM images for Y123 film grown on YSZ with 30 (right) and 150 (left) shots of Ag.

films fabricated under optimized PLD conditions [7]. This implies that the ablation conditions used for our samples are not optimized. The results of the J_c enhancement by the Ag nano-dots for our samples indicated that surface modification with Ag nano-dots is another factor controlling the performance of the Y123 films in addition to other physical deposition conditions.

To clarify why the Ag nano-dots play a role in the J_c enhancement, we checked for any differences in the surface morphologies of our films using both SEM (Fig. 3) and AFM. We found that for 0, 15, 30, 60 Ag shots, the film surface morphologies are indistinguishable under SEM and AFM. The surface morphologies for the film with 150 Ag shots look similar to all the others, however, this sample exhibited a clear feature of growth islands and nano-holes forming trenches between the growth islands. Typical AFM surface images of two Y123 films grown on STO with 30 and 150 Ag shots are shown in Fig. 4.

Characteristic of AFM for all films is the island structure, with an island diameter of typically 100–500 nm, separated by deep trenches consisting of nano-size holes, which can be clearly visualized under high magnification SEM as well. For 150 shots, the AFM showed a higher density of growth islands with smaller diameters and nano-holes than all the other films. However, as the J_c increases monotonically with Ag shots in our samples, it seems that the surface morphology has no direct relationship with the J_c enhancement. Therefore, we have to check the phases, orientations and crystallinity of our films.

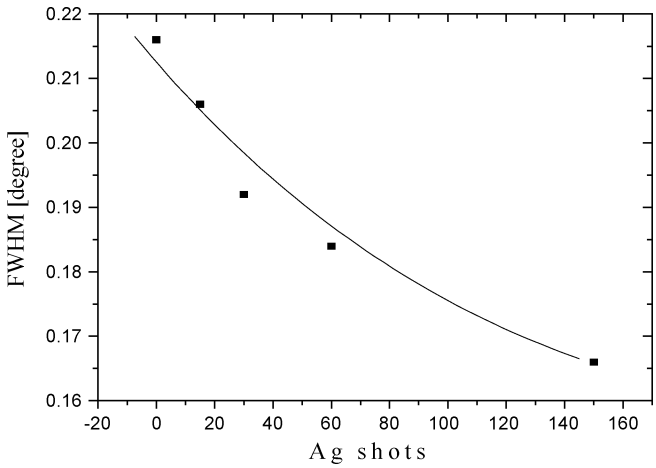

Fig. 5. FWHM (005) peak of Y123 films on YSZ vs. Ag shots.

All the XRD results revealed that the out-of-plane orientation of the Y123 films in all samples is strong, with only the (00l) reflections being present. Therefore, it seems that there is no difference in the orientation of the samples. However, if we check the full width at half maximum (FWHM) for the (005) reflection peak for different samples, it is found that the values of the FWHM decrease as the Ag shots increases, i.e., the (005) peak becomes sharper with Ag dots, indicating the improvement of crystallinity in the films or improvement of the (00l) orientation of crystal grains. Therefore, we believe that the increase of J_c with Ag nano-shots should be ascribed to the improvement in the out-of-plane alignment caused by Ag nano-dot modification to substrate surfaces (Fig. 5).

However, although the FWHM became sharper for films with $n = 60$ and 150, the J_c dropped as $n > 30$. In addition, the higher density of growth islands implies that the 150 Ag shot films should have extra linear defects acting as pinning centers for flux pinning compared with the other samples, as it has been reported that each growth island provides one linear defect in PLD Y123 film on STO substrates [8], [9]. The possible reason behind the decrease in J_c for n greater than 30 is likely to be that the angle between adjacent grains, in other words, the angle between a or b axis of adjacent grains may have increased for $n > 30$. It has been well established that the J_c drops as the angle between grains increases [10]. The larger the misalignment angles of a or b, the smaller the J_c values.

For the films grown on LAO and STO, the microstructures under SEM and AFM have exactly the same trends as we have observed for films grown on YSZ. No distinguishable features were found for $n = 0, 15, 30, 60$. Differences in SEM and AFM images are only present for $n = 150$. It was also found that the FWHM decreased monotonically with gradually increasing n, indicating improvement of the c-alignment of films with n. Due to improvement of the c-alignment, the J_c is naturally expected to increase with the number of Ag shots. This in fact is clearly seen from the Ag shot dependence of J_c over a wide temperature range and in both zero and high fields for the films grown on STO, as shown in Fig. 6. It can be seen that the J_c increases monotonically with the number of Ag shots. For films grown on LAO, the general trend of J_c with the number of Ag shots is that J_c increases with n as shown in Fig. 7. Zero field J_c at 77 K

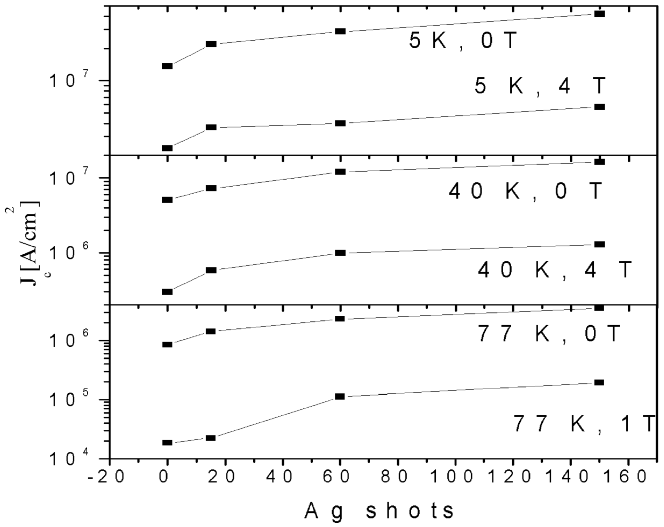

Fig. 6. Jc vs the number of Ag shots for the film grown on STO.

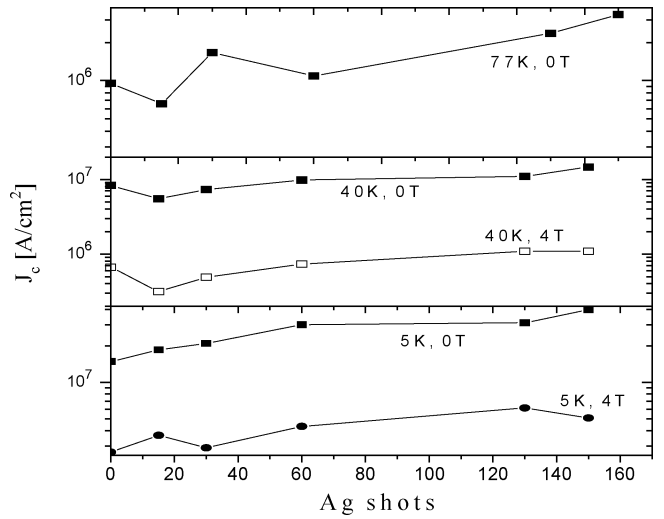

Fig. 7. J_c vs the number of Ag shots for the film grown on LAO.

increased from 10^6 to 3.3×10^6 A/cm^2, and from 1.5×10^7 up to 4×10^7 A/cm^2 for 5 K and zero field as n increased from zero to 150. However, we see the same fluctuation of J_c with $n < 60$ for most temperatures and fields except for 5 K and zero field. The reasons for these J_c fluctuations are not clear at this moment. It might be possible that the Ag-nano-dots may have different ways to settle onto the surface of the LAO substrate, most likely due to the Ag dots having different chemical activity compared to dots on both YSZ and LAO. This might affect the distribution or diameter of Ag-dots when the number of Ag shots is less than 60. Despite the J_c fluctuation for $n < 60$, the Ag nano-dots indeed improved the c-alignment of the films and in turn increased the J_c values at both low field and high field if the number of Ag shots was greater than 30.

In summary, the Y123 films grown on single crystal substrates whose surfaces were modified with Ag nano-dots revealed improved ab alignment and hence the increase of J_c with the increase of the density of Ag dots.

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