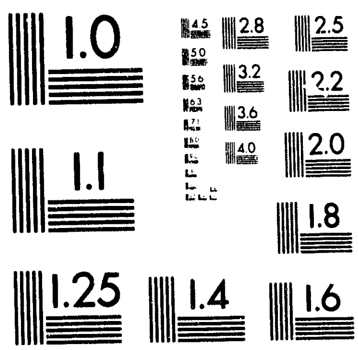
1.0
4.5
5.0
5.6
6.3
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

Note: This is a preprint of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the author(s).

Submitted to the *Conference on Laser Ablation (Cola '93)*
April 19–22, 1993

Particles on Surfaces of Laser Ablated $YBa_2Cu_3O_{7-\delta}$ Films

X.-Y. Zheng,* D. H. Lowndes, Shen Zhu,* and R. J. Warmack

*The University of Tennessee
Knoxville, Tennessee

Solid State Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6056
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

PARTICLES ON SURFACES OF LASER ABLATED $Y_1Ba_2Cu_3O_{7-\delta}$ FILMS

X.-Y. Zheng, D. H. Lowndes, Shen Zhu, and R. J. Warmack
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6123

ABSTRACT

Pulsed laser deposition of $Y_1Ba_2Cu_3O_{7-\delta}$ films grown at heater temperature of 720 and 800 C on $SrTiO_3$ and MgO substrates with thickness ranging from a nominal 5 unit cells to 200 nm were studied by STM and SEM. The size and density of particles present in the films were found to depend on film thickness, growth temperature and substrate. STM images indicate a correlation between film growth mode and particle density: the onset of big particles comes after the growth mode changes from layer-like to island growth.

INTRODUCTION

Laser ablation deposition is a simple yet powerful technique. It is used for the growth of high quality $Y_1Ba_2Cu_3O_{7-\delta}$ thin films because of an important advantage of this technique that the stoichiometry of the target, even with multiple components, is preserved in the film. One of the major drawback of this technique, however, is the presence of particles of various sizes on and embedded in the films. These particles that consist of clusters and droplets are believed to originate from the explosive nature of the laser-solid interaction. Their presence in thin films is usually highly undesirable especially for the growth of superlattice structures.

A number of techniques are employed to reduce the density of particles present in the films[1,2]. Most of those techniques are based on the fact that the velocities of the particles are inversely related to their sizes (masses)[1], and are a factor of 10 to 100 slower than that of the ions and atoms. Substantial reduction of particle density is achieved by using of mechanical shutters[1] and by intersecting the ablated beam of a second, crossed and delayed, beam that either destroys or pushes aside the particles[2].

Up to now emphasis is on the creation of fewer particles by conditioning the target and minimization of particles before their arrival at the film surface. It is also known that the size, shape, and number density of particles depend strongly upon laser conditions and wavelength. Little attention has been paid to what happens at the film surface. In this paper we report the dependence of particle size and density on the growth modes and conditions of the $Y_1Ba_2Cu_3O_{7-\delta}$ films.

EXPERIMENTAL

Details of the general conditions for film growth were reported elsewhere[3]. Briefly, $Y_1Ba_2Cu_3O_{7-\delta}$ films were grown on $SrTiO_3$ and MgO substrates by pulsed KrF (248 nm) excimer laser ablation of bulk $Y_1Ba_2Cu_3O_{7-\delta}$ targets in 200-mTorr oxygen pressure at heater temperatures of 720°C and 800°C. The substrate surface temperature is estimated to be about 50°C cooler.

The oxygen pressure was increased immediately after deposition and the films were cooled to room temperature at 10 C/min. in ~400 Torr oxygen. The deposition rate was ~0.05 nm per laser pulse and the laser was operated at a pulse rate of 2.2 Hz.

Three sets of films on $SrTiO_3$ substrates were prepared for the study of particle size and density dependence on film thickness and growth temperature. Set 1 consists of four samples of thickness 5, 10, 15, and 20 nominal unit cells. Set 2 and Set 3 contain two more samples of thickness 50 and 100 nominal unit cells. For each set the substrates were placed side-by-side on the heater surface which was 7 cm away from the target, and films of different thickness were grown in a single run to insure the same target condition. The thickness of the films was controlled by shutters which were placed 1 cm away from the substrates. The first two sets, grown at 800 C and 720 C, respectively, were prepared as the following: films started to grow at the same time, and shutter was applied when individual film reached the desired thickness. One concern about this procedure is that thinner films stayed long time at the growth temperature and oxygen pressure without receiving additional materials including particles, and diffusion may have taken place in those films that resulted in a reduction of particle density. To eliminate possible effects of diffusion, a third set of films grown at 800°C was prepared applying shutters in a reversed order: shutters were placed to block the substrates initially, and removed one-by-one in such a way that films started to grow at different times and reached the desired thickness simultaneously at the end of deposition. Rise of heater temperature up to 10°C was observed when shutters were applied because they prevented the convention of the heat from the heater surface. This may have caused some inaccuracy in the results.

RESULTS

Pairs of $Y_1Ba_2Cu_3O_{7-\delta}$ films grown on $SrTiO_3$ and MgO substrates, respectively, but in the same growth run were studied with SEM. Substrate dependence of particle size and density was observed. Figs. 1(a) and 1(b) are images taken from such a pair of films with a thickness of nominal 24 unit cells and growth temperature of 800°C. The particles seem to appear in two distinct sizes in both of those films. The particle density in the film on MgO, Fig. 1(a), is considerably higher than that in the film on $SrTiO_3$, Fig. 1(b). However, the size of the bigger particles in Fig. 1(b) is larger than that present in Fig. 1(a). Difference in particle shapes is evident from the images. Similar results were observed in other pairs of films of different thickness and growth temperature. However, the difference in particle size and density is not apparent in thick (~200nm) films.

SEM images of $Y_1Ba_2Cu_3O_{7-\delta}$ films on $SrTiO_3$ of the same thickness but with different growth temperature show that particle density is greater in films grown at lower temperature. A typical example is given in Fig. 2(a) and 2(b), showing the difference in particle size and density in nominal 20 unit-cell-thick films grown at 800°C and 720°C, respectively. The difference in particle density increases with film thickness in the 5-100 unit cells range. Samples of 200 nm thickness show no apparent difference in particle density. The difference in particle size is also thickness dependent. Similar result was observed in films on MgO substrates grown at those two temperatures. Temperature dependence of particle density and size is determined by comparing samples from different growth run. Observation error may have resulted due to possible difference in target conditions.

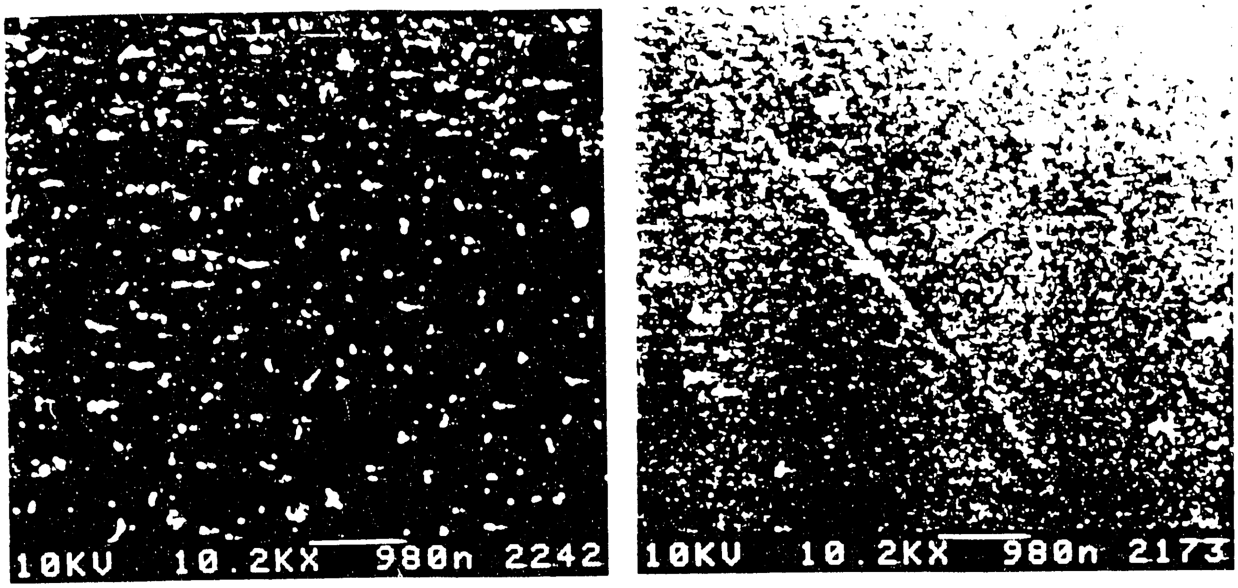

Fig. 1. SEM images of $Y_1Ba_2Cu_3O_{7-x}$ films grown at 800 °C on (a) MgO and (b) $SrTiO_3$ substrates.

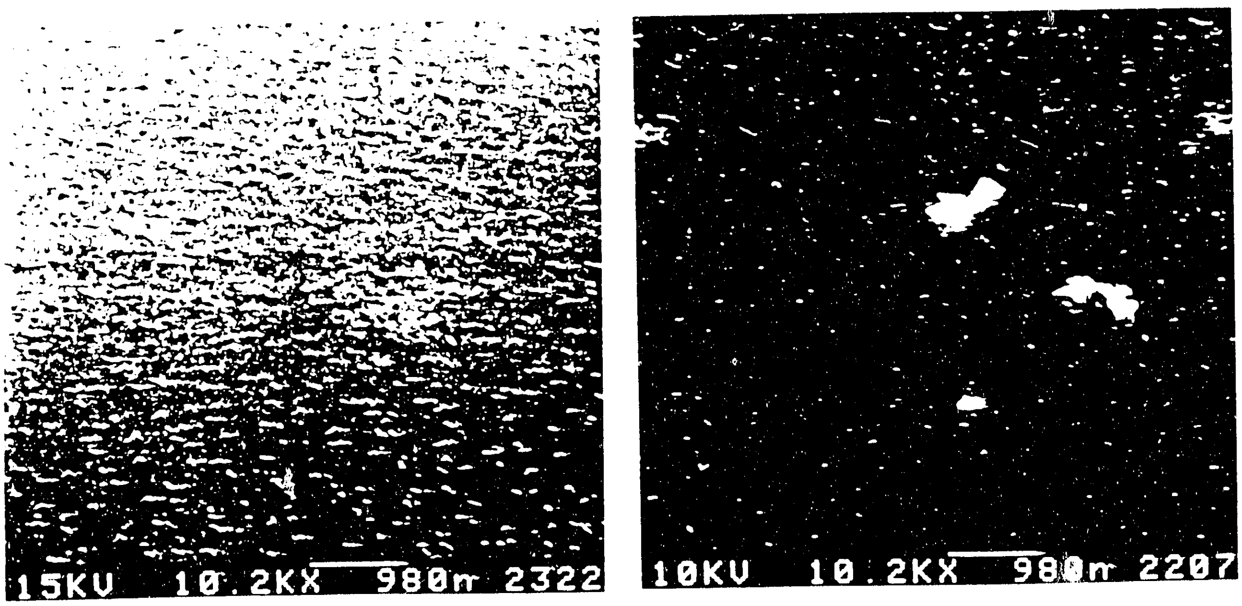

Fig. 2. SEM images of $Y_1Ba_2Cu_3O_{7-x}$ films grown on $SrTiO_3$ substrates at (a) 720 °C and (b) 800 °C. Images were taken with 50° sample tilt.

The most important observation is the thickness dependence of particle size and density. Figs. 3(a) and 3(b) show the particles in films from Set 2 (720 C) of thickness 20 and 50 unit cells, respectively. There seem to be two types of particles. The first type, of smaller size, are present in all thickness (5-100 unit cells), as shown in Fig. 3(a). Their size decreases, but density increases with thickness, however, the density increases with thickness. The other type of particles, the larger ones with more variation in size, emerge at larger thickness (50 unit cells), as shown in Fig. 3(b). Their density also increases with thickness as is evident comparing the 50 and 100 unit-cell samples of the same set. SEM images of 200 nm thick films grown at the same temperature as Set 2 show low density of the larger particles and no appearance of the small sized particles. This seems to indicate that as the thickness is further increased the small particles vanish, and the density of the larger particles become constant. Again, error may occur when comparison is made between samples from different growth run. Another feature that is apparent especially in films grown at 800 C is the position of the small particles. They often stay in holes as seen in Fig. 2(b).

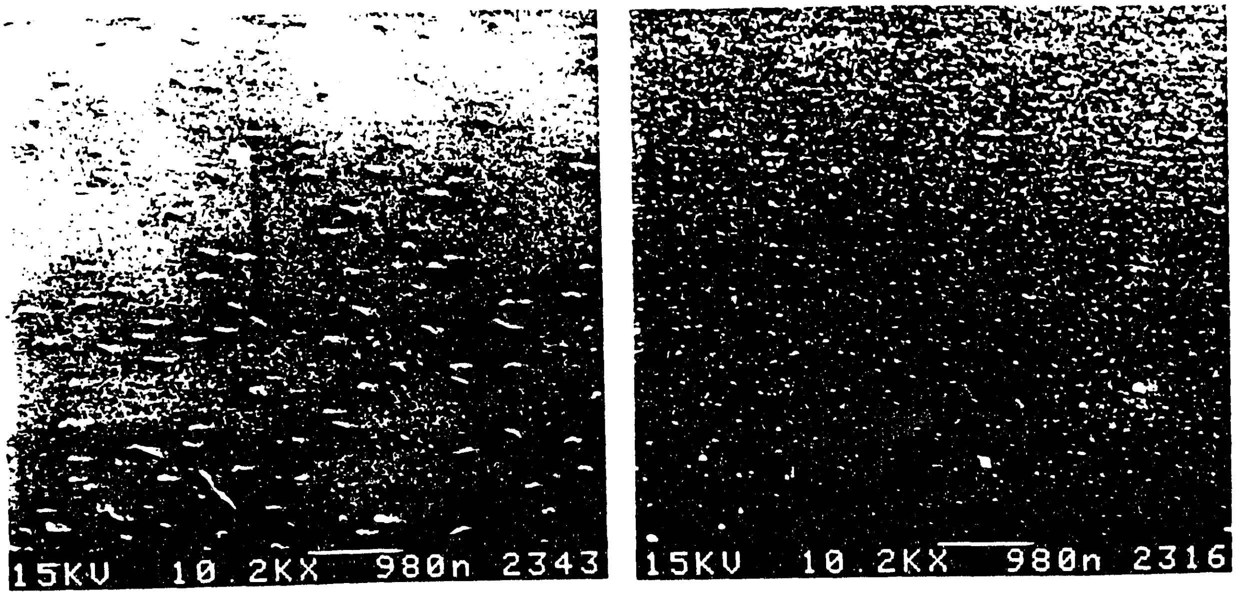

Fig. 3. SEM images of (a) 20 unit-cell-thick and (b) 50 unit-cell thick $Y_1Ba_2Cu_3O_{7-\delta}$ films grown at 720°C on $SrTiO_3$ substrates. Images were taken with 50° sample tilt.

STM images show the same density of particles as SEM images, but offer some insight due to its high resolution. One of the sample, a 15 unit cell thick film from Set 1, happens to have regions with small miscut angle (~1-2). Fig. 4(a) and Fig. 4(b) represent STM images taken from the normal regions and regions with small miscut, respectively. High density of particles are present in the normal regions as seen in Fig. 4(a). The particles in Fig. 4(a) appear to have the same shape. This is an artificial tip effect, i.e., the STM tip images instead of the particle images are present due to the small size of the particles. Titled plates of $Y_1Ba_2Cu_3O_{7-\delta}$ layers in Fig. 4(b) indicate the small miscut of the substrate. The growth mode in this region is different. The particle density as seen in Fig. 4(b) is much lower.

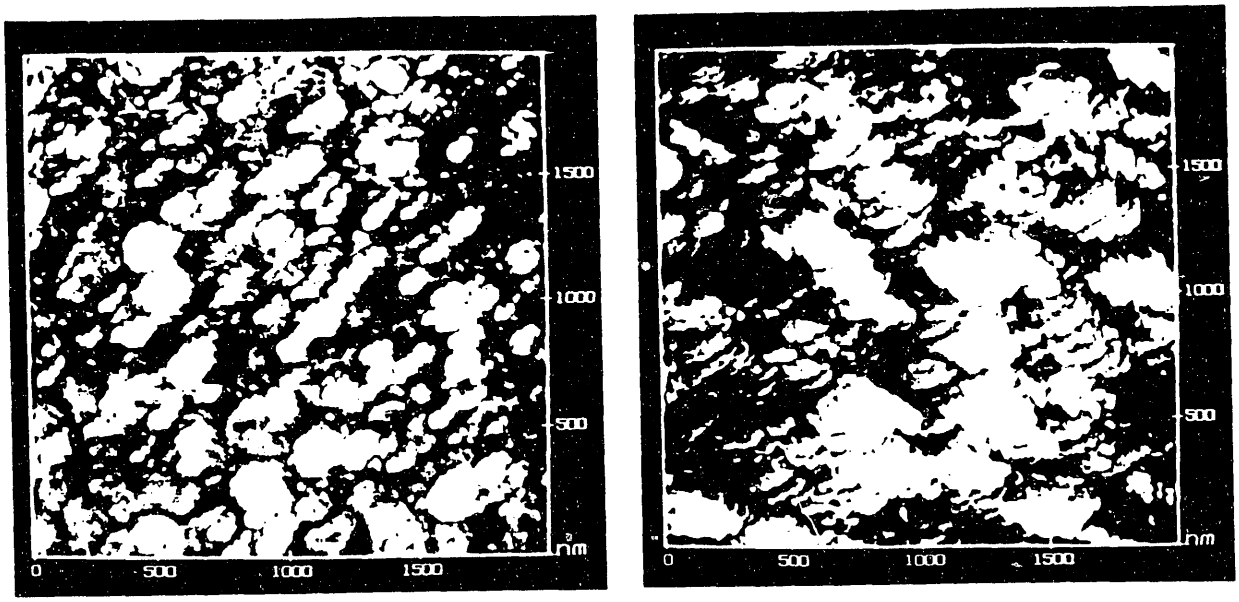

Fig. 4. STM images of of a $Y_1Ba_2Cu_3O_{7-\delta}$ films grown at 800°C on $SrTiO_3$ substrates(a) a normal region and (b) a region with miscut.

DISCUSSION

As we know, thin films grow in three basic modes: layer-by-layer growth, island growth, and layer-by-layer followed by island growth. Previous STM studies[3-5] revealed that $Y_1Ba_2Cu_3O_{7-\delta}$ films grow in the third mode. For films on $SrTiO_3$, the switching from layer-like to island growth takes place at thickness of about 5-10 unit cells for growth temperature of 720°C, and 12-20 unit cells for 800°C[5]. Initially, the island density is high and size is small. When the islands grow bigger they coalesce with each other, resulting in a reduction of density. Their density and size become roughly constant at large thickness (~200nm). The growth mode of $Y_1Ba_2Cu_3O_{7-\delta}$ films on miscut substrates with small title angle is very different[6]. Because edges of the steps exposed on the surface provide spots for fast growth, nucleation of islands is unfavorable, and layer-like growth continues at large thickness. Our results presented above indicate that the size and density of the particles depend strongly on the surface conditions of the films.

Assuming the same flux of particles of various size from the target for each shot at all time of the growth period, the presence of particles of certain size and density at different film thickness seems to indicate that only suitable types of the particles that match the surface conditions of the films are accepted on the surface. As is evident from Fig. 2(b) and STM images, particles stay in lower regions where the surface energy is the lowest. When a film is in the layer-like growth stage, most area is flat, and there are fewer spots with lower surface energy that accept particles. At the early stage of island growth, the onset of big particle is prevented because the density of the islands is high, and the space between them is small. Big particles are accommodated by holes large and deep enough, which is possible only after the islands become larger and their density smaller due to coalescence.

Another strong evidence of growth mode dependence is the STM images shown in Figs. 4(a) and 4(b). As mentioned above, regions in Fig. 4(b) provide plenty sites for fast growth. The lower particle density in those regions may be contributed to two factors: the layer-like growth mode associated with miscut surface provides fewer spots (holes) to adopt particles; diffusion of deposited materials in those region may be faster due to many available sites for growth, and so does the decomposition of the particles.

To conclude, particle size and density present in pulsed laser deposited $Y_1Ba_2Cu_3O_{7-\delta}$ films depend not only on laser and target conditions, but also on growth stages of the films. Variation of the film surface energies due to factors such as surface morphology, growth temperature and types of substrates determines the particle size and density.

ACKNOWLEDGMENT

This research was sponsored by the Division of Materials Science, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. D. Lubben, S. A. Barnett, K. Suzuki, S. Gorbakin, and J. E. Greene, *J. Vac. Sci. and Technol.* **B3**, 968 (1985); T. Venkatesan, X. D. Xu, R. Muenchausen, and A. Pique, *MRS Bulletin* **17**, 54 (1992).
2. G. Koren, R. J. Baseman, A. Gupta, M. I. Lutwyche, and R. B. Laibowitz, *Appl. Phys. Lett.* **56**, 2144 (1990).
3. Shen Zhu, D. H. Lowndes, X.-Y. Zheng, D. P. Norton, and R. J. Warmack, *Mat. Res. Soc. Symp. Proc.* **237**, 541 (1992).
4. X.-Y. Zheng, D. H. Lowndes, Shen Zhu, J. D. Budai, and R. J. Warmack, *Phys. Rev. B: Rapid Commun.* **45**, 7584 (1992).
5. X.-Y. Zheng, D. H. Lowndes, Shen Zhu, and R. J. Warmack, *Mat. Res. Soc. Symp. Proc.* **263**, 41 (1992).
6. D. H. Lowndes, X.-Y. Zheng, Shen Zhu, J. D. Budai, and R, J, Warmack, *Appl. Phys. Lett.* **61**, 852 (1992).

DATE

FILMED

11 / 3 / 93

END