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Post Deposition Heat Treatment Effects on Ceramic Superconducting Films Produced by Infrared Nd:YAG Pulsed Laser Deposition

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1. Introduction

Pulsed laser deposition (PLD) has become a potential method in fabricating highly quality superconducting thin films suitable for electronic applications such as in Josephson junctionbased electronics and in second generation coated conductors [11, 12, 14, 20, 23]. PLD of high *T_c* superconductors generally utilize excimer lasers in the ultraviolet (UV) range [6, 11]. However, excimer lasers use toxic gases such as Cl and F for excitation. In contrast, flash lamp pumped Nd:YAG laser can provide stable power and better beam profile [14, 20]. Nd: YAG lasers are also easy to operate and have low maintenance costs [2, 14, 20]. To date, the third harmonic (355 nm) and fourth harmonic (266 nm) of the Nd:YAG has been used to grow high quality high-Tc superconducting films [12, 14, 20].

In UV PLD of Bi-Sr-Ca-Cu-O films, the substrates are usually heated to 800^{0} C followed by in-situ and ex-situ post heat treatments in gas atmospheres [1, 13, 22, 29]. Reports have shown that Bi- content of the film is greatly influenced by the substrate temperature and can be highly deficient at higher temperatures [1, 29]. In some cases, heat treatment during deposition results in the contamination of the film especially on Si substrates [6]. PLD of $YBa_2Cu_3O_{7-\delta}$ using UV lasers produce films with T_c of 90 K require substrate heating ranging from 700- 800^{0} C in a background O_2 gas (pressure of ranging from 100 to 200 mTorr) [6, 7, 32]. This is usually done since Y-Ba-Cu-O is highly dependent on oxygen content. This process is either performed in-situ or ex-situ and part of the post heat treatment [4, 18]. These results implies that post heat treatment is necessary to homogenize the composition of the film and improve the critical temperature T_c [1, 4, 19]

Recently, we reported the fabrication of micron thick $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) and Yttrium doped Bi-22Y2 through PLD with a 1064 nm Nd:YAG laser [9, 10]. The films underwent heat treatment outside the PLD growth chamber to produce flat and highly c-axis oriented films with stoichiometries identical to the targets. In the case of Bi-2212, the measured T_c is



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only about 58 K and for Bi-22Y2, the highest T_c is 90.5 K at 25% Y concentration [9, 10]. Y substituted Bi-2212 films grown by IR PLD show drop in magnetoresistance and improved critical current density J_c [3].

The primary motivation of these previous works is to use the existing Nd:YAG laser in PLD experiments to avoid the complicated optics and gas systems of an excimer laser based PLD. Also, when fundamental wavelength of the Nd-YAG laser is used for deposition, films with the same chemical composition as the starting material can be fabricated, and therefore it is versatile in the deposition of multicomponent films. The film properties can be adjusted through heat treatment steps after deposition.

In this chapter, we examine effect of post heat treatment on the the morphology, composition, crystallinty of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ prepared by IR Nd:YAG PLD.

2. Infrared Nd:YAG laser ablation and post heat treatment

The laser system used in this study is a Q-switched Nd:YAG (Spectra Physics GCR 230) operating at 1064 nm at 10 Hz repetition rate with 8 ns pulsed duration. The deposition was performed in a stainless steel vacuum chamber continuously evacuated to maintain a pressure of 10^{-2} mbar. The solid state sintered target is placed 30 mm from the substrate and was rotated for uniform laser ablation. The Bi-Sr-Ca-Cu-O films were grown on (100) MgO substrate with laser fluence of 5.5 J/cm², while Y-123 films on (100) *SrTiO*₃ single crystal substrates with laser fluence of 2.0 J/cm². These values of fluences are typical for PLD of Bi-Sr-Ca-Cu-O and Y-Ba-Cu-O [5, 8, 23, 33]. The deposition was performed without substrate heating and no other gasses from external sources were introduced in the chamber during deposition.

For Bi-Sr-Ca-Cu-O films, two heat profiles in ambient air was performed. Some were partial melted at 880 °C and some were heated at 940 °C for 15 minutes and rapidly quenched to room temperature. Both of the heat profiles are seconded with annealing at 850 °C for 2 hour. In the case of Y-123, three heat treatment steps were performed, first the films were re-sintered at 900 °C for 12 hrs followed by heating at 1000 °C for 15 minutes and rapid thermal quenched to room temperature. The last heat treatment involves, heating on a tube furnace with oxygen at 930 °C for 12 hours, and annealed at 450 °C for 2 hours in ambient air.

Scanning electron microscopy (SEM) were used to examine the surface morphological features and composition of the films. Film thickness was determined by SEM cross- sectional imaging. X-ray Diffraction (XRD) were used to investigate the composition and crystal properties of the film. To verify superconducting property of the films, linear four point probe resistance measurement were performed.

3. Post deposition heat treatment effects

3.1. Bi-Sr-Ca-Cu-O films

SEM surface micrographs of partial melted and rapidly quenched Bi-2212 films grown with 5.2 J/cm^2 energy fluence at 10^{-2} mbar chamber pressure for 180 minutes is shown in Figure 1. Relatively smooth and flat films were obtained using partial melting and annealing treatment as can be seen in figure 1a. At higher magnification (film 1c), layering inherent to the

Bi-Sr-Ca-Cu-O is observed. The average thicknesses of the films are 9 μ m. In figure 1b, films heated at 940 °C for 15 min and the rapidly quenched films show pronounced layering and terraces of Bi-Sr-Ca-Cu-O. This makes the film rougher compared to partially melted Bi-2212 films. The rapidly quenched films is thinner compared to partial melted films with an average thickness of about 2 μ m. Both films show small amount of spheroidal particulates after heat treatment [10].



Figure 1. SEM surface micrographs of Bi-2212 films subjected to (a, c) partial melting and (b,d) rapid quenching. Both films were subquently annealed.

XRD measurements on the partial melted and rapidly quenched Bi-2212 films is shown in figure 2. The peaks are indexed using the card file no. 41-0317. Both films are highly c-axis oriented with minimal Bi-2201 impurity. However, sharper XRD peaks are observed for films subjected to partial melting indicating higher crystalline quality.

The rough morphology of films subjected to rapid quenching at very high temperature is due to very fast cooling of the Bi-2212 material. It has been observed that IR PLD Bi-2212 films require partial melting and annealing to allow uniform diffusion and migration of Bi-2212 materials on MgO substrate forming smoother film [10]. This attributed to the micron-size spheroidal grains trasferred on the substrate by the IR laser during deposition [10]. Hence, heat treatment is required to facilitate growth, flatten and densify the material producing much thinner films.

Figure 3 shows the resistance vs temperature measurement on the partial melted Bi-2212 films with transition temperature, T_c of about 79 K. In our previos report, partial melting with subsequent annealing for 10 hours results into T_c of only about 58 K. The shorter annealing



Figure 2. XRD pattern of Bi-2212 film grown by IR- PLD Nd:YAG subjected to post heat treatment. Both films are highly c-axis oriented films are achieved with post heat treatment. Sharper peaks were observed for partially melted films.

time improved the transition temperature. It has been reported that longer annealing time reduces oxygen content in the films [23]. In the case of rapidly quenched films, the measured T_c show almost similar value. Although rapid quenching produce rougher films it still posses T_c comparable with the partial melted films.

3.2. Y-Ba-Cu-O

Figure 4 shows the SEM micrographs of (a) a representative as- deposited films grown using $2.0J/cm^2$ laser energy fluence at 10^{-2} mbar deposition pressure for 180 minutes, and rapidly quenching films in ambient air at 1000 °C for 15 minutes, (b)without, and (c,d) with oxygen annealing. The as-deposited films show spheroidal grain with an average size of about 0.6 μ m. The surface of the film also contain micro-cracks extending to about 10 μ m in length. The surface of both rapidly quenched Y-123 films were covered with rectangular grains of different sizes. In fig. 4b, the rectangular grains have an average size of about 1.4 μ m ±0.3 x 1.3 μ ±0.3, while film subjected to oxygen annealing (fig. 4c) have an average size of 1.7 μ m ±0.4 x 1.8 μ m ±0.2. The rectangular particles also grow on top of another particle (indicated by circle). Some of the rectangular particles also have different orientation including growth perpendicular to the basal plane (arrow) and parallel to the substrate surface (dashed arrow). In most UV PLD of Y-123, these rectangular shaped grains are presumed to be a- axis oriented [16, 17, 21, 28]. This is observed especially when a solid- state sintered target is used for the



Figure 3. Resistance as a function of temperature of Bi-2212 film prepared by 1064 nm Nd:YAG pulsed laser deposition with post heat treatment.

deposition. However, the sizes which are comparably smaller compared to IR Nd:YAG Y-123 films [16].

At a higher magnification (fig. 4d), the surface of the oxygen annealed Y-123 film show that the grains interconnect laterally forming larger particulates with extended grain boundaries (indicated by squares). This is a common feature of Y-123 films especially when solid state sintered targets are used as the material source for the deposition [15, 21]. While the heat treatment helps in densifying the grains, it also aids in coalescence of grains and forming an alignment of the material relative to the substrate orientation [10]. The appearance of rectangular grains could be a result of incongruent melting of Y-123 at rapid thermal heating at 1000 °C and the thickness of the films. The surface of the film also indicates that the film is not fully melted at that temperature. This is partly due to micron-sized grains transferred by IR laser pulses that needs higher temperature to completely melt. This also attributed to the high melting temperature of Y-123 of about 1200 °C. Hence, we can infer from the SEM image that film is at the initial stage of growth.

The observed morphology of the Y-123 film is due to the micron sized particulates generated by IR PLD. It has been reported that large YBCO particulate are difficult to merged into YBCO films completely especially in the surface of a thick film where the mobility and heat exchange rate are lower than that in the substrate surface, hence they will hinder the c-axis growth of surrounding film [34]. Larger YBCO grains in the as-deposited films could provide sites for the nucleation of a-axis grains [25, 34]. Since large chunks of the target are able to arrive on the substrate surface forming inherently thick films, preferential a-axis formation is observed when you subject to heat treatment. In contrast, UV PLD generates ultrafine particles that lands on heated substrate forming thinner film with c-axis orientation. We are also unable



Figure 4. SEM micrograph of Y-123 film deposited by IR Nd: YAG PLD (a) as- deposited, and rapidly quenched at 1000 °C for 15 minutes to room temperature in ambient air (b) without and (c) with oxygen annealing. The window in (c), magnified by a factor of 2 at 2 μ m scale, is shown in (d).

to see micro-cracks initially observed in the as-deposited films. This is due to annealing that result to removal of pores and enlargement of grains [9, 10]. The growth of a-axis grains also contribute to dispersion of micro-cracks [15].

Figure 5 shows the XRD spectra of Y-123 films without and with oxygen annealing. The XRD pattern for both films are composed of c-axis and a-axis oriented Y-123 grains. It contains no other diffraction peaks from the precursors of the Y-123 material. This indicates high phase purity of the film. The reflection corresponding to (006) and STO (200) is hard to distinguish due to the small lattice mismatch of Y-123 with STO (about 2%). The value of c-lattice parameters for film not subjected to oxygen annealing is about c= 11.77 while for oxygen annealed film, c= 11.68 . The value of the c-lattice for oxygen annealed film is similar to the oxygen rich Y-123 (c= 11.68) [30] . The variation in c-lattice can be attributed to the decrease in the fraction of oxygen gas in YBCO material [25]. Hence, oxygen annealing is necessary for the as-deposited films.

The mixture of a-axis and c-axis is due to the thickness of the film and partly due to incongruent melting of Y-123 at 1000 °C. It has been reported that Y-123 films possess mixture of a-axis and c-axis growth as a result of increasing film thickness [27]. In contrast to previous reports that the critical thicknesses to obtain crack free Y-123 is about 2.2 μ m [31], we do not observed micro cracks on heated films [26]. This is due to granularity of the heated films suggesting that a higher temperature is needed to fully melt the films. Future work must be done by using higher melting temperature in oxygen atmosphere in order to improve the surface morphology and T_c of the Y-123 films.



Figure 5. XRD spectra of post heated Y-123 films. Both films were rapidly quenched in ambient air, while (b) includes oxygen annealing

Figure 6 shows the resistance vs. temperature measurement on Y-123 films. Without oxygen annealing the film shows semiconducting behavior (fig. 6a) [24]. This attributed to oxygen deficiency in the film. In contrast, the oxygen annealed film (fig. 6b) shows superconducting transition temperature T_c of about 70 K. This is comparably low with the observed transition temperature with the bulk target of about 89 K.

The a-axis outgrowths are typically observed in the c-axis oriented thick films. The a-axis outgrowth inhibits transport of the superconducting currents in the films resulting into a low value of T_c [17]. The films are also granular introducing weak links at the grain boundaries affecting T_c . This is the main reason of having low T_c values for the films. Although the lattice parameters indicate fully oxygenated Y-123 lattice, the morphology of the films greatly affects superconducting property of the film. Hence, micron thick YBCO films deposited using IR laser needs ex-situ oxygen annealing to improve the T_c of films. Although the a-axis oriented Y-123 films present always a lower critical temperature than that of a c-axis oriented films (about 10 K lower), the study of the a-axis oriented films are useful for sandwich type Josephson device applications [5].

In summary, the heat treament greatly influence the growth and surface morphology of IR PLD films. Since the films are deposited on un-heated substrates, the habit of the material upon heat treatment becomes an important parameter in choosing heat treatment profiles. Layering and grain movement during high temperature melting can be reduced by exposing the film at temperatures closer to the melting temperature and introduction of annealing steps in an environment conducive for uniform coalesnce and intake of oxygen. The temperature



Figure 6. Resistance vs. temperature measurement on Y-123 films heated in (a) ambient air, (b) oxygen ambient. The oxygen annealing helps in forming superconducting films. The low value of T_c is attributed to granular surface morphology of the film and also to the oxygen annealing profile used.

used for Y-Ba-Cu-O is low enough to see the initial stage of growth and will allow us to implement a heat profile that will melt and provide sufficient oxygen on the film.

4. Conclusion

The post heat treatment studies on IR Nd:YAG PLD films is an important stage in developing the technique to be a competitive and alternative technique in producing high T_c superconducting films for electronic applications. The use of non-toxic lasers to deposit coupled with appropriate heat treatment profiles to grow the films is an efficient tool in minimizing the complicated control of parameters in conventional PLD of high T_c superconductor materials. It is envisioned that IR Nd:YAG PLD technique can grow high quality materials with critical current densities useful in the production of films for second generation coated conductors.

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