Dependence of the Structural, Electrical and Magnetic Properties of the Superconductive YBCO Thin Films on the Deposition Rate

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Abstract. In this study, YBCO thin films on single crystal LaAlO₃ (100) substrates have been grown using DC inverted cylindrical magnetron sputtering technique and the effect of the deposition rate on these films is investigated. Three different deposition rates are used to produce superconducting YBCO thin films with 150 nm of thickness on (100) LaAlO₃ single crystal substrate at 780°C. The samples are analyzed in detail by means of XRD, R-T, χ-T, M-H and AFM characterizations and also the critical current densities (Jc) are derived from the magnetic hysteresis curves using the modified Bean formula [1]. The critical current density at 50 K was found to be in the range of 3.10⁷ A/m² to 8.10⁷ A/m² with a deposition rate between 2nm/min and 1.2nm/min. A correlation has been obtained so that as the film deposition rate increases, the surface smoothness and crystalline quality of the films significantly deteriorate, resulting in a significant decrease in Jc.

1. Introduction

After the discovery of high temperature superconductivity [2], enormous effort has been put forward to produce thin film forms using superconductive materials with epitaxial structures. A great percentage of these studies have been focused on determining the required physical growth conditions of thin films for electronic device applications and optimization of these conditions [3].

Among the high temperature superconductors, YBa₂Cu₃O₇₋δ (YBCO) is a widely used material which has a transition temperature over the boiling point of liquid nitrogen. Further advantages of YBCO over others are non-poisonous components, high phase stability, high quality of crystallization, high flux pinning, low surface resistance and single step deposition oxygenation in-situ process [3]. The main disadvantage of YBCO is the strong dependence of its crystal structure and superconducting properties on the level of oxygenation during the growth process. This critical dependence on the oxygen content determines a transition from tetragonal phase which is non-superconductive to orthorhombic phase which is superconductive. There are various techniques for epitaxial growth of YBCO thin films, such as chemical vapor deposition (CVD) [4], pulsed laser deposition (PLD) [5], molecular beam epitaxy (MBE) [6], laser molecular beam epitaxy (L-MBE) [7], DC- and RF– sputtering [8,9]. The widely used sputtering technique of producing large area films in industry should be viable for the industrial production of YBCO thin films. As of now, this technique is a popular method in laboratories for small-scale fabrication of YBCO films [10]. Li et al. [11] showed that films produced by inverted cylindrical magnetron sputtering system (ICMS) are better than those produced by non-magnetron inverted cylindrical sputtering at the same conditions. Non-magnetron system bombards the film surface with energetic ions so that there occurs re-sputtering. Geerk et al. [12] also expressed that during the planar magnetron sputtering; film surface is bombarded by negative ions having the same amount of energy of argon ions which bombards the target surface. As a result, ICMS
system is very suitable for obtaining high quality and homogenous thin films and this system is widely used.

There are many parameters which affect the superconducting properties of YBCO thin films. These are substrate preparation, target condition, gas mixture, growth temperature and deposition rate. Degardin et al. [13] have reported that the substrate preparation is a major step for the elaboration of good quality superconducting films. The choice of the substrate material is of primary importance because the crystal formation of the coated thin films parallels the crystal structure of the substrate. Therefore, there should be accordance between the substrate and the crystal lattice of high temperature superconductor together with a similar thermal expansion and also no chemical interaction on the boundary surface [3]. Taniwaki et al. have reported that the change of substrate temperature affects the quality of crystallization of thin films [14]. Also, Selinder et al. reported that sputtering pressure effects the film crystallization [15], and Liu et al. reported that the increase of deposition rate will negatively affect the superconducting transition properties, and also will increase the lattice disorder concentration and make a rough surface in the resulting YBCO thin films [16]. And also, Avci et al reported the variations in YBCO thin film properties for different substrate coatings [17].

In this study, we systematically investigated the YBCO thin film preparation on substrates of single crystal (100) oriented LaAlO$_3$ by ICMS technique with different deposition rates. Other parameters were kept fixed at optimized values derived in previous studies [17, 18]. The YBCO samples were studied by structural (XRD, AFM), electrical (R-T) and magnetic ($\chi$-T and M-H) measurements.

2. Experimental

YBa$_2$Cu$_3$O$_{y-\delta}$ thin films of 150 nm thickness were deposited onto 10x10x0.5 mm$^3$ (100) LaAlO$_3$ substrates by using DC Inverted Cylindrical Magnetron Sputtering (ICMS) system. The sputtering device, as well as the YBCO target, was commercially purchased from Hitec-Materials [19]. The substrate surface cleaning is a very important process for the epitaxial thin film growth. In this study, the substrates were cleaned with ultrasonic cleaner in acetone for 1 hour and subsequently in isopropyl alcohol for 1 hour. After cleaning, the substrate was glued to the substrate holder of sputter system with silver paste. The thin film deposition was carried out at a fixed temperature of 780°C. Argon and oxygen gas pressures were maintained at 0.15 mbar during the deposition. In order to obtain different deposition rates 1.2, 1.6 and 2.0 nm/min. for different samples, we varied the plasma power from 55 to 75 watts, simultaneously adjusting the deposition times for obtaining a fixed film thickness of 150 nm.

After the deposition, the crystalline structure and surface morphologies of the YBCO thin films were analyzed by x-ray diffraction (XRD) and atomic force microscopy (AFM). The superconducting transition temperatures of the YBCO thin films were measured by dc four-probe point method. Current reversal technique was used to eliminate the effects of voltage offsets. The ac magnetic susceptibility ($\chi$-T) and magnetization (M-H) measurements have been carried out with commercial SQUID magnetometer (Quantum Design Inc., MPMS-5). The samples were attached to the sample holder so that their plane was perpendicular to the applied magnetic field during the measurements. M-H loops were measured at 50 K and critical current densities ($J_c$) were calculated based on the extended Bean critical state formula [20], 

$$ J_c = 20\Delta M / [a(1-a/3b)] $$

where $\Delta M$ is the width of magnetization loop in emu/cm$^3$, a and b ($a<b$) are dimensions of the YBCO samples in cm.

3. Results and Discussion

3.1. R-T Measurement

Temperature versus resistance change of the YBCO thin films which were deposited on the LaAlO$_3$ substrates with the rates of 2.0, 1.6 and 1.2 nm/min are shown at the Fig. 1. The transition temperature of all the samples ($T_{\nu0}$) is at around 90 K but the value of the $\Delta T$ changes. Transition to superconductive phase occurs at a narrower $\Delta T$ with the decreasing deposition rates. Very small positive value of R(0) resistance or the exact zero value of R(0) states that the normal phase of the samples show better metallic properties [17]. The different resistance values of the different deposition rates of YBCO superconductive thin films at normal phases can be seen at Figure 1 clearly. The low value of room temperature resistance and bigger ratio of R(300)/R(100) show that there will be a
greater critical transition temperature [21]. Samples with the deposition rates of 2.0, 1.6 and 1.2 nm/min in that order have ratios of $R(300)/R(100)$ as 2.83, 3.09, 3.13. It is clearly seen that the deposition rate of 1.2 nm/min has the highest ratio with the smallest normal state resistance, so that it supplies the highest zero resistance temperature $T_c (R=0)$.

![Resistance vs. temperature curves of the YBa$_2$Cu$_3$O$_{7-\delta}$ YBCO thin films by different deposition rates](image)

**Fig. 1.** Resistance vs. temperature curves of the YBa$_2$Cu$_3$O$_{7-\delta}$ YBCO thin films by different deposition rates

### 3.2. Susceptibility Measurement

Susceptibility measurement is widely used for the determination and characterization of the polycrystalline HTSCs. Usually two peaks is observed [22]. In Fig. 2 and 3, responses of real ($\chi'$) and imaginary ($\chi''$) AC magnetic susceptibilities can be seen depending on the different magnetic field (1 Oe and 4 Oe) with frequency values of 80 Hz, 586 Hz and 986 Hz. It is clearly seen from Fig. 2 that as the deposition rate and AC magnetic field amplitudes increase, $\chi'' (T)$ shifts to lower temperature values and broadens over temperature. It is well known that the amount of the shift as a function of the field amplitude is proportional to the strength of the pinning force. The sharpness of these curves proves the homogeneity of the films whereas the increasing deposition rates show a loss at the susceptibility curves. So, it can be safely said that slower deposition rates result in the best homogeneous film. And also it can be seen at Fig. 2 that increasing magnetic field causes a wider region for the transition and increasing deposition rate results in a more sensitive behavior for the magnetic field. On the other hand, in figure 3, it is clearly seen that samples are not affected from changing frequency that much of magnetic field so that there has been no significant change at the sharpness of the curves. Many researchers have observed that the AC magnetic susceptibility of high $T_c$ superconductors is weakly dependent on the frequency [23-25] and depends strongly on the AC magnetic field amplitude $H_{ac}$ [26-28]. And also, by looking at the figure 3, it’s clearly seen that as frequency increases, AC magnetic susceptibility curves slightly shift to the higher temperature.
Figure 2. Magnetic susceptibility vs. temperature curves of YBCO thin films on different deposition rate for 1 and 4 Oe magnetic field

Figure 3. Magnetic susceptibility vs. temperature curves of YBCO thin films on different deposition rate for different frequencies

3.3. Magnetization Measurement

At the Fig. 4, the magnetization curves of the samples at the 50K can be seen. It is clearly seen that the sample with the slowest deposition rate traps more magnetic field. In a relation with these results, calculated critical current density values depending on the Bean formula can be seen at the Fig 5. At
the brief sight of the critical current densities at 50K, samples with the deposition rate of 1.2nm/min are significantly different with that of the samples with the deposition rate of 2nm/min.

![M(H) curves of YBCO thin films on different deposition rates](image1)

**Figure 4.** M(H) curves of YBCO thin films on different deposition rates

![Jc curves of YBCO thin films on different deposition rates](image2)

**Figure 5.** Jc curves of YBCO thin films on different deposition rates

### 3.4. XRD Measurement

In figure 6, XRD results of the thin films in the range of 2θ=10°-60° can be seen. YBCO structure deposited as a thin film can have two different alignments due to its anisotropic formation. In this case, a right angle alignment with the substrate surface is called as c-axis alignment. There are many causes which affect the alignment of the YBCO thin films and the most important is the structure of the substrate used and its alignment. LaAlO3, SrTiO3 and MgO substrates with (100) alignment are mostly used substrates [21]. Also, the quality of the crystallization of thin films strongly depends on the consistency of the substrate lattice. The accordance between the substrate and films in the means of lattice, improve the crystallization of the films [21]. As seen at the figure 6, produced thin films have
c-axis alignment. The sample grown on (100) single crystal LaAlO$_3$ substrate with a relatively low deposition rates of 1.2 nm/min shows a highly aligned c-axis orientation. The peak intensities and the amount of c-axis orientation are decreasing as the deposition rate increases to 2nm/min Full width at half maximum of the (005) peak show the growth along the c-axis. With smaller FWHM of the films there will be better c-axis alignment according to substrate [16] and this value has a most important role on the superconductive properties of the films [21]. In our samples, the YBCO (005) peaks had FWHM values equal to 0.35°.

![Figure 6. XRD measurement of samples](image)

3.5. AFM Measurement
Our investigation has yielded a correlation between the deposition rates the surface morphology parameters, such as the surface roughness parameter, by employing AFM studies. Higher deposition rate creates more energetic ions so that more massive parts can be plucked from the target. Higher deposition rate and shorter time for the deposition causes non homogeneous distribution of these parts on the substrate. This situation creates rougher surface. Three dimensional images and analysis of the roughness can be seen at Fig. 7. Samples deposited with the rates of 2nm/min, 1.6 nm/min. and 1.2 nm/min. have surface roughness values of 6.071 nm, 5.459 nm and 4.944 nm. In this analyze, in accordance with the previous ones [29], 1.2 nm/min deposition rate yields with the decreased surface roughness.
Figure 7. Surface roughness images of YBCO thin films with different deposition rates.

4. Conclusion
In this study, we grew thin films using ICMS technique on LaAlO$_3$ substrates. We have selected the deposition rate parameter, which is very important among the other parameters such as the choice of substrate and its temperature, total oxygen pressure during the deposition and partial pressure of the oxygen. We obtained three different samples. Upon experimenting with the structural and magnetic properties of the samples, we have found that although all the samples showed respectively useful good properties, the sample with low deposition rate showed a smoother surface and higher $c$-axis orientation and also contained more capacity for flux trapping which is accompanied by more resistance to the applied magnetic field.

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