$YBa_2Cu_3O_{7-\delta}$ Thin Film Growth on Different Substrates by Pulsed Laser Deposition

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Abstract

There were a lot of research on $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting materials and this material still draw attention. In this research, thin films of commonly used superconducting YBCO ceramic material, grown on $LaAlO_3$ (LAO), MgO and $SrTiO_3$ (STO) substrates as thin films, which have different thermal expansion constants and lattice parameters, by Pulsed Laser Deposition (PLD) technique. 150 mTorr partial Oxygen pressure, 5 cm substrate to target distance and 800 °C substrate temperature used for all thin film growths. Thin films characterized for film quality and microstructure with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques. Analysis of these thin films showed that highly *c* oriented *(00l)* YBCO thin films obtained with LAO and STO substrates, which are more compatible than MgO for YBCO growth.

Keywords: $YBa_2Cu_3O_{7-\delta}$ thin films, YBCO, $LaAlO_3$, MgO, $SrTiO_3$, Superconductivity, Pulsed Laser Deposition, PLD

1. Introduction

Superconducting materials show almost zero resistance under a critical temperature and commonly used for high magnetic field generation, magnetic levitation, electric transport and magnetic imaging systems. YBCO material contains Yttrium, Barium, Cupper and Oxygen elements in its structure with oxygen deficiency and it is a very important Type-2 high temperature superconductor. YBCO shows superconductivity at 93 K which is over the boiling point of liquid Nitrogen (77 K) (Wu *et al.* 1987). YBCO ceramic has a three-layered perovskite structure without any toxic or volatile components. YBCO crystal in orthorhombic structure has superconducting properties with lattice parameters of a = 3.82 Å, b = 3.89 Å and c = 11.67 Å (Kim and Lee 1999). Thermal expansion constant of YBCO is given as 13.4 $x10^{-6}$ $°C^{-1}$ (Kawashima *et al.* 1998). Thin films of YBCO finds usage in micro-electronic devices such as detector and filters (Li *et al.* 2017), especially as Superconducting QUantum Interference Devices (SQUIDs) for magnetic flux change detection (Lee *et al.* 1995) and bolometers for electromagnetic radiation detection (Aboudihab *et al.* 1994). It is possible to grow thin films on many different substrates, but for a selective directional crystal growth, it is essential to choose a substrate with lattice match and similar thermal expansion constants, without any chemical reaction between substrate and deposition material. Substrate selection is very important for high quality superconducting thin films, suitable for device applications. Substrate effect should not be ignored, since it has significant role in determination of the properties of the thin film it supports and specific applications require various substrates for different purposes (Phillips 1996).

Pulsed Laser Deposition (PLD) is a favored physical vapor deposition technique used for growth of high quality single crystal thin and thick films of one element to complex structures (Lee *et al.* 1991; Bierleutgeb and Proyer 1997). This technique has many variables that affect the film growth substantially. (Chrisey and Hubler 1994; Proyer and Stangl 1995; Proyer *et al.* 1996). In order to obtain a good film, variables like; spot size, laser energy, deposition pressure, deposition gas, number of pulses, pulse frequency, heating and cooling rates, target rotation and raster speeds, substrate rotation speed and substrate to target distance has to be optimized (Chrisey and Hubler 1994; Duhalde *et al.* 1998; Kim and Lee 1999). It is

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possible to grow sandwich structures with multiple target holders by PLD. Contaminations can be prevented with in-situ annealing of the samples inside the PLD chamber.

In this study, previously optimized YBCO thin film growth parameters (Yurtcan *et al.* 2013) were used for growth of the YBCO thin films on 3 various substrates; $LaAlO_3$ (LAO), MgO and $SrTiO_3$ (STO) having different lattice parameters. Thin films of YBCO on different substrates characterized and best thin film that is closest to single crystal for device applications was determined.

2. Experimental Details

All of the substrate materials for YBCO growth purchased from MTI Corporation as wafers and sliced substrates. Wafers and substrates were 1 side polished and (*100)* oriented single crystals. LAO sliced from 3 inch diameter wafer into 15 x 5 mm substrates with a diamond saw in our laboratory. MgO sliced from 2 inch side length square wafer into 10 x 10 mm square substrates with a Disco DAD322 Automatic Dicing Saw in East Anatolia High Technology Application and Research Center (DAYTAM). STO substrates purchased as 10 x 10 mm square substrates and used as they were. Table.1 shows the lattice parameters, dielectric and thermal expansion constants of these substrates.

Table.1. Physical properties of the substrates.

	Lattice Parameters	**Dielectric Constant**	**Thermal Expansion Constant**
LAO	a = b = 3.790 Å	~ 25	10 x10^{-6} °C^{-1}
MgO	a = b = 4.216 Å	9.8	12.8 x10^{-6} °C^{-1}
STO	a = b = 3.905 Å	~ 300	10.4 x10^{-6} °C^{-1}

Compared to MgO's lattice, LAO and STO lattice parameters are very close to YBCO's *a* and *b* values. On the other hand, thermal expansion constant of MgO is more compatible than LAO and STO for YBCO thin films.

Prior to the substrate pasting into substrate holder, all the substrates cleaned with acetone and methanol for 8 minutes in an ultrasonic bath to prevent organic contamination on substrate surfaces. Cleaned substrates pasted into substrate holder with Ted Pella Inc. Leitsilber 200 Silver Paint and then left for drying about 30 minutes.

YBCO target prepared by cold pressing 9.5 grams of high purity YBCO powder (Matech Inc.) with a density of 6.30 g/cm^3 into 1 inch die set. YBCO pellet than sintered at 905 °C for 20 hours in atmosphere for hardening (Yanmaz *et al.* 2009).

Thin films grown by Neocera Inc. "Complete P180 PLD Laboratory" system with a 248 nm wavelength KrF excimer laser "Coherent Compex Pro 102" in Atatürk University. Fixed growth parameters were 5 cm substrate to target distance, 150 mTorr O_2 partial pressure, 800 °C substrate temperature and 10 Hz frequency. (Yurtcan 2011; Yurtcan *et al.* 2013). Vacuum chamber evacuated by a turbo molecular pump in order to prevent contamination of thin films during growth. Substrates heated to 800 °C and the chamber pressure increased to 150 mTorr with 99.999% high purity O_2 gas by a mass flow controller. Prior to crystal growth, a shutter used to cover the substrate and laser fired upon YBCO target to clean target surface. After that, shutter opened and 6000 laser pulses used for crystal growth. As soon as crystal growth finished O_2 gas flow switched off and substrate temperature reduced to 400 °C with 10 °C/min ramp rate to prevent cracking between substrate and the thin film. When the temperature reached 400 °C, Oxygen gas given into the chamber and pressure increased to 300 Torr. Samples annealed in-situ at these conditions for an hour. After annealing, substrate temperature reduced to 200 °C with 10 °C/min ramp rate and then natural cooling took over. After temperature reached to 90 °C, chamber opened to atmosphere and then the samples removed from the chamber.

Crystal structure of the thin films determined by a PANalytical Empyrean X-Ray Diffractometer (XRD). Morphological structures and elemental analysis conducted with a Zeiss Sigma-300 Scanning Electron Microscope (SEM) - Energy Dispersive Spectroscopy (EDS) system.

3. Results

Thickness of the thin films are very small compared to substrate thickness. For this reason, we used "Grazing Incidence" XRD method (GIXRD) in order to avoid peaks from the substrates in thin films. YBCO is an air sensitive material and exposure to the air causes reflectivity profile to change (Han *et al.* 2003). GIXRD measurements for all thin films conducted with a grazing incidence angle of 0.5°. XRD peaks belonging to *c* oriented (*00l*) YBCO peaks (Zhai *et al.* 2001) and

XRD patterns of YBCO grown onto different substrates at the same conditions are given in Figure.1.

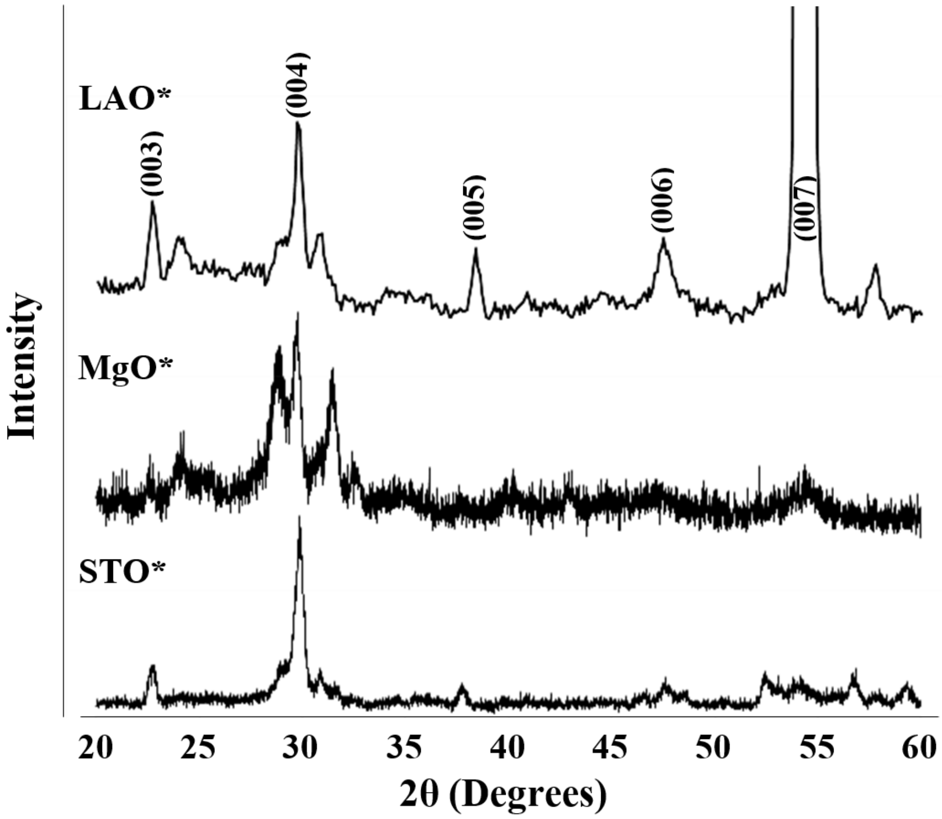
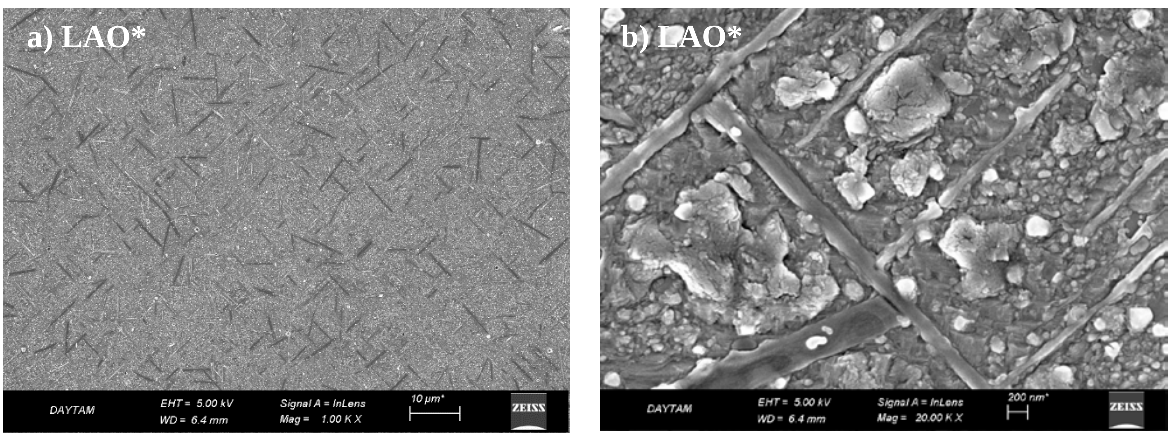


Figure.1. XRD patterns of YBCO grown onto different substrates.

It is clear from Figure.1 that YBCO thin film grown onto MgO substrate have random orientation compared to other substrates. Thin film over STO substrate is highly *c* oriented with maximum peak intensity in *(004)* direction. YBCO thin film grown onto LAO substrate have significantly high intensity in *(007)* direction with all *(00l)* directions present between 20 to 60 degrees (2θ) range. This result makes YBCO/LAO thin film top crystallinity over the other studied samples.

Surface morphologies of YBCO thin films analyzed with a SEM device and surfaces of different substrates are given with 1000 and 20000 times magnifications, in Figure.2, respectively.



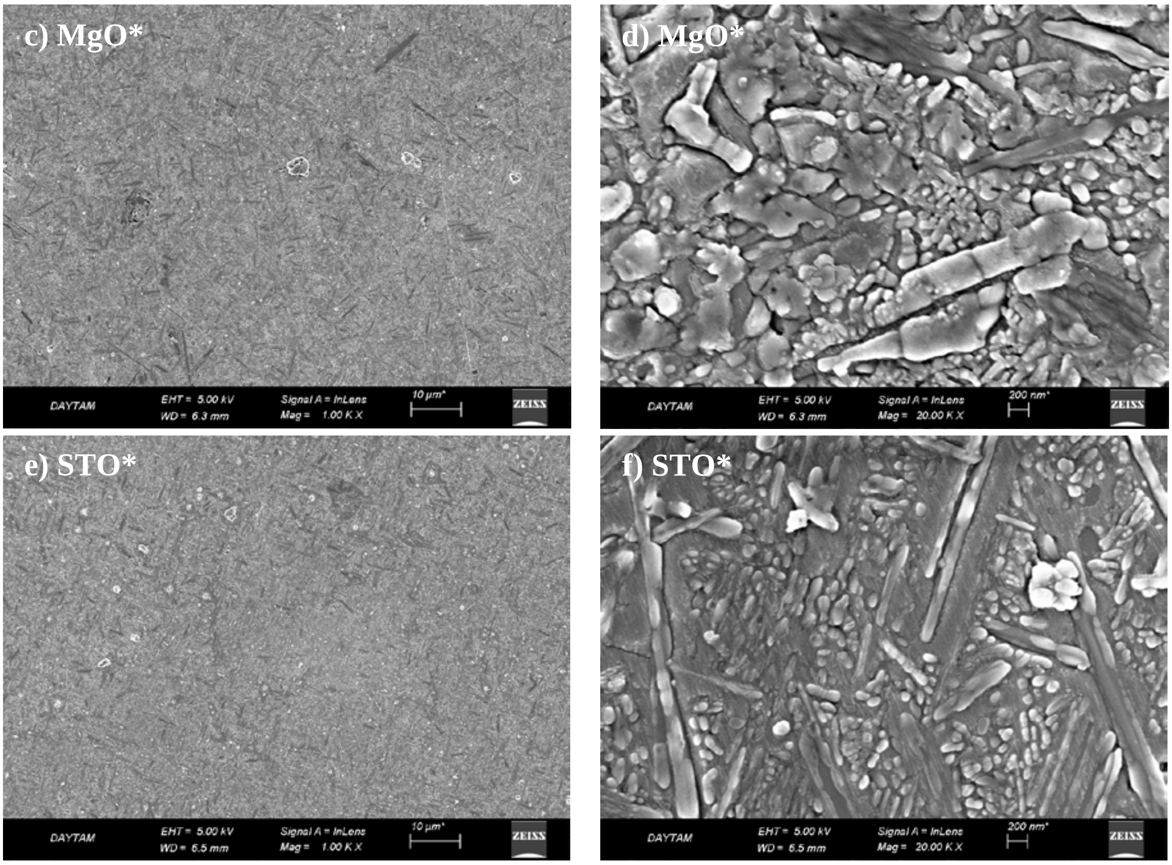


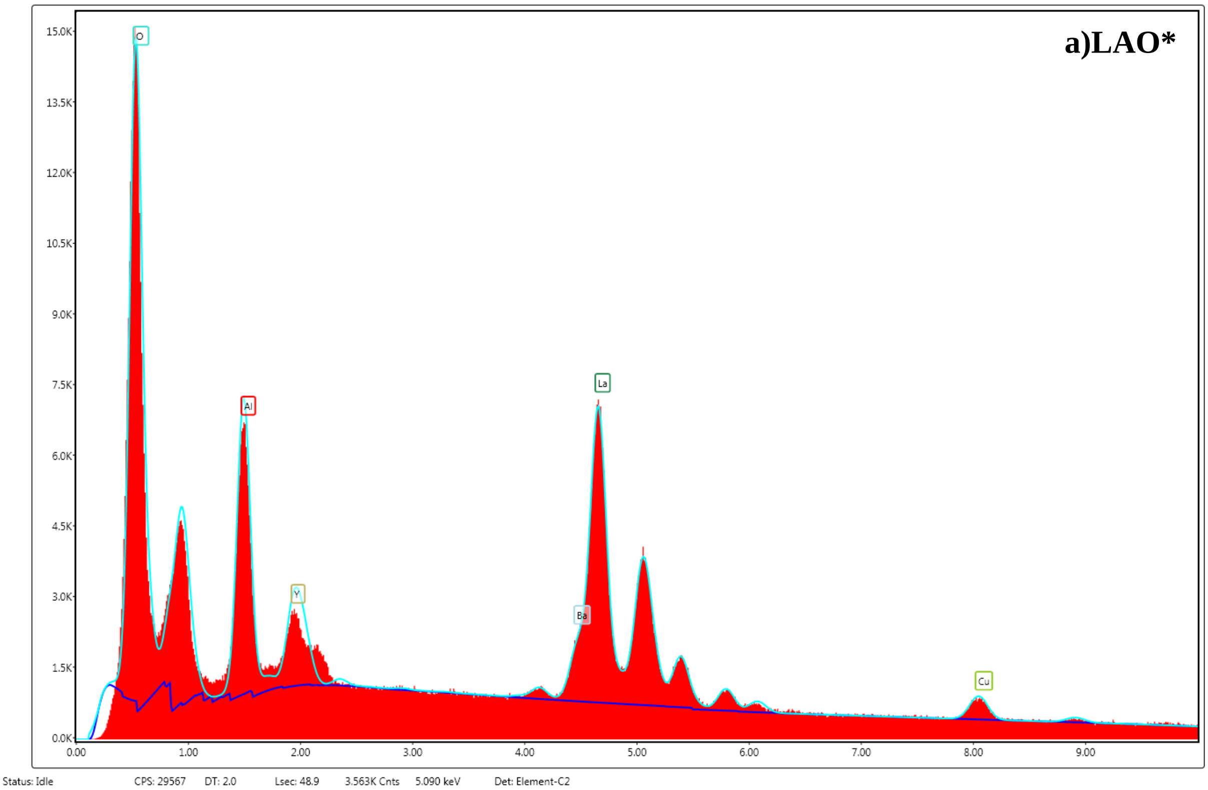
Figure.2. SEM images of YBCO thin films on different substrates **a)** LAO* (1000x), **b)** LAO* (20000x), **c)** MgO* (1000x), **d)** MgO* (20000x), **e)** STO* (1000x) and **f)** STO* (20000x)

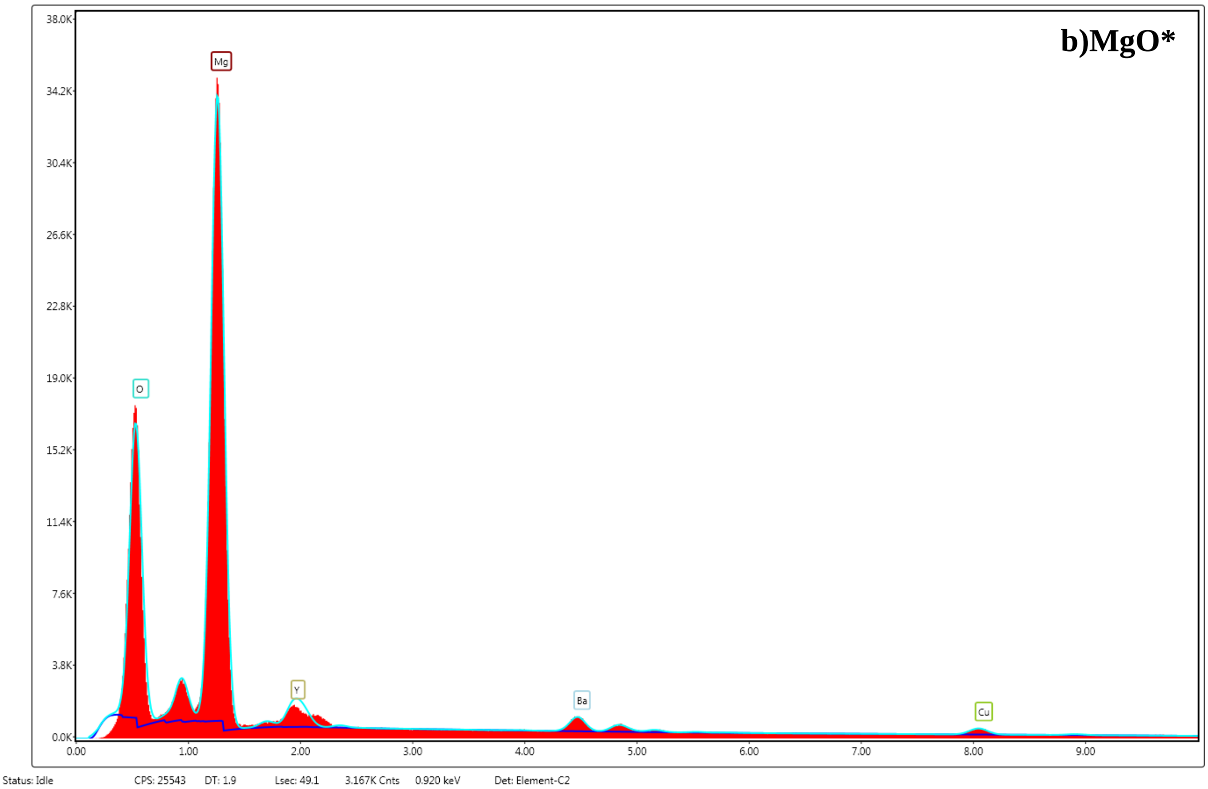
Comparison of YBCO thin film surfaces with 1000 times magnification show that smallest droplet size and count caused by PLD techniques nature, observed in LAO compared to other substrates. All YBCO thin films on different substrates have rods parallel to the surfaces. Length of the rods in LAO substrate vary between 5-10 µm (Figure 2.a) with 100-300 nm thickness (Figure 2.b). Rods are shorter and random in MgO substrate; also, there are holes and more droplets over the surface (Figure.2.c). Thickness of each rod on MgO vary in its own compared to other substrates (Figure.2.d). There are more and bigger droplets over STO compared to LAO substrate with the length of 2-4 µm rods (Figure.2.e). Those rods over STO substrates have 100-250 nm thickness (Figure.2.f). SEM images reveal that none of the thin films has cracks caused by thermal expansion coefficient difference between substrate and YBCO thin films.

Elemental information of thin films on different substrates analyzed by EDS of the SEM system. All substrate and thin film elements present in analysis results (Figure.3) and their weight and atomic percent ratios shown in Table.2.

Table.2. Weight and atomic percent ratios of the thin films.

LAO*			MgO*			STO*		
Element	**Weight %**	**Atomic %**	**Element**	**Weight %**	**Atomic %**	**Element**	**Weight %**	**Atomic %**
O K	17.9	53.2	O K	27.9	42.5	O K	29.7	64.7
Al K	10.5	18.5	Mg K	51.9	52.1	Sr L	32.3	12.9
Y L	4.2	2.2	Y L	4	1.1	Y L	4	1.6
Ba L	8.8	3	Ba L	9.2	1.6	Ba L	6.6	1.7
La L	51.4	17.6	Cu K	7	2.7	Ti K	22.5	16.4
Cu K	7.3	5.5				Cu K	4.9	2.7


a)LAO*
O
Al
Y
Ba
La
Cu
15.0K
13.5K
12.0K
10.5K
9.0K
7.5K
6.0K
4.5K
3.0K
1.5K
0.0K
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
Status: Idle CPS: 29567 DT: 2.0 Lsec: 48.9 3.563K Cnts 5.090 keV Det: Element-C2


b)MgO*
Mg
O
Y
Ba
Cu
38.0K
34.2K
30.4K
26.6K
22.8K
19.0K
15.2K
11.4K
7.6K
3.8K
0.0K
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
Status: Idle CPS: 25543 DT: 1.9 Lsec: 49.1 3.167K Cnts 0.920 keV Det: Element-C2

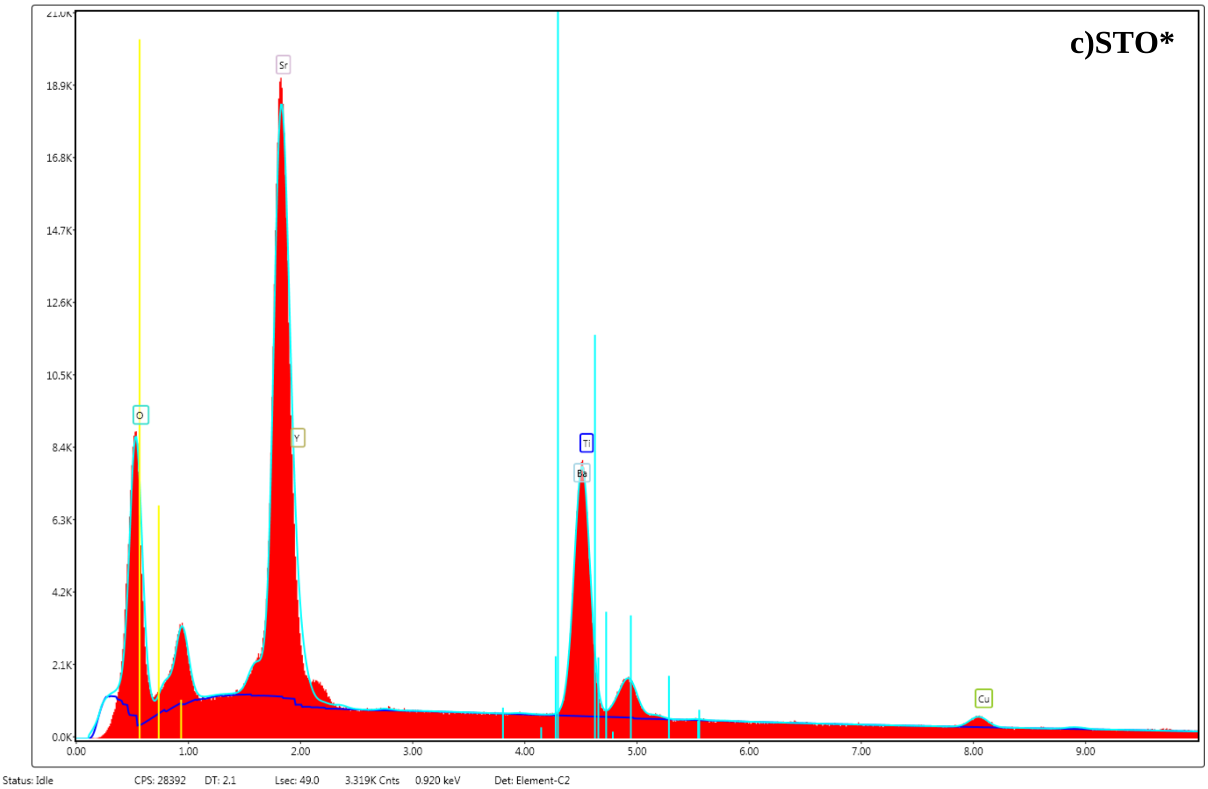


Figure.3. EDS analysis of thin films on **a)** LAO, **b)** MgO and **c)** STO substrates.

EDS analysis show that, YBCO thin film on LAO substrate have maximum Y, Ba and Cu atomic percent ratios. This result followed by STO substrate and MgO substrate has the lowest atomic percent for YBCO.

Thin film thickness measured with a KLA Tencor P-7 Stylus Profiler. Measured thickness was between 234-286 nm with an average of 260 nm. This result shows that approximately 0.43 Å / pulse achieved by PLD method with these fixed conditions.

As a result, YBCO thin films on LAO and STO substrates grown more successfully than MgO substrate. Lattice mismatch between YBCO and MgO single crystal are +10% in *a*-direction and +8% in *b*-direction, respectively. This result shows that lattice mismatch is very significant in thin film growth via PLD technique.

4. Conclusions

We have grown YBCO thin films on LAO, MgO and STO substrates at the same conditions by PLD technique and samples were in-situ annealed. XRD patterns of YBCO thin films revealed that thin film grown on MgO does not have any certain orientations. On the other hand, YBCO thin films grown on LAO and STO have high *c* orientations with very high intensity in LAO's *(007)* and high intensity in STO's *(004)* peaks. Comparison of SEM images of the YBCO thin films showed that thin film grown on LAO has the least and smallest droplets on the surface. All three thin film surfaces have rods with different sizes parallel to the surface. EDS analysis showed that Y, B and Cu elements are least found in thin film grown on MgO substrate. Compared to each other, LAO substrate has the best and MgO substrate has the worse thin film growth.

This study shows that substrate materials' lattice parameters affect the thin film properties significantly in PLD technique. MgO is a very sensitive material to moisture and if it is required as a substrate material for YBCO thin film growth, a suitable buffer layer is highly recommended between YBCO and MgO substrate. We strongly recommend LAO as YBCO thin film substrate for its close lattice match to YBCO. In addition, it is shown that, STO is a good substrate candidate for YBCO thin films, in case a substrate with a higher dielectric constant is required for device applications.

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