

GROWTH STUDY OF Y-BA-CU-O ON BUFFER LAYERS AND DIFFERENT SUBSTRATES MADE BY ULTRASONIC SPRAY PYROLYSIS

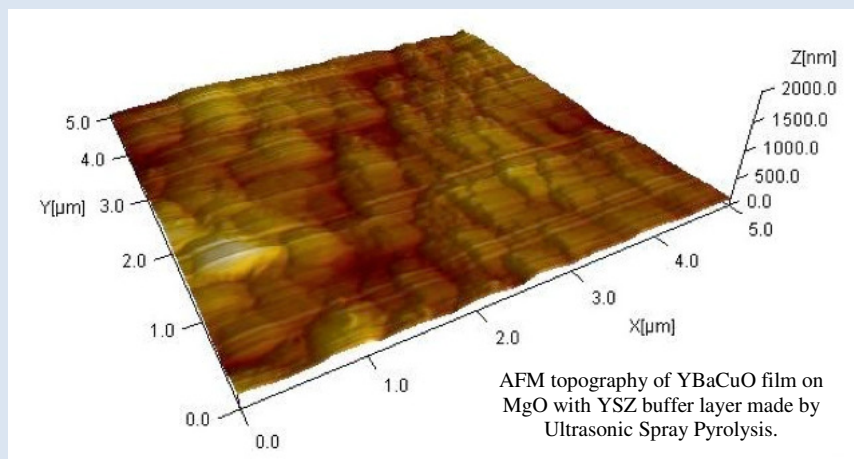
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ABSTRACT

Atomic Force Microscopy (AFM) was used to observe the growth stages of both buffer layers and Y-Ba-Cu-O films on three different substrates: Si (100) and MgO (100) for crystalline ones and fused silica for the amorphous type. In order to compare the benefits of buffer layers, YSZ was grown on the three different substrates and AFM topographies were made at each stage of growth: Bare substrate, YSZ films on bare substrates, Y-Ba-Cu-O/YSZ films and Y-Ba-Cu-O on bare substrates. An Ultrasonic Spray Pyrolysis system was used to deposit all the films and layers. Films grown on buffer layers present smoother surfaces than those grown on bare substrates.

Keywords: Ultrasonic Spray Pyrolysis, YBaCuO, YSZ, AFM, Roughness

ESTUDIO DEL CRECIMIENTO DE Y-BA-CU-O SOBRE CAPAS BUFER Y DIFERENTES SUSTRATOS HECHOS POR ROCÍO PIROLÍTICO ULTRASÓNICO

RESUMEN

Se utilizó Microscopía de Fuerza Atómica (AFM) para observar por etapas el crecimiento de capas búfer y películas de Y-Ba-Cu-O sobre tres sustratos diferentes: Si (100) y MgO (100) como sustratos cristalinos y cuarzo como sustrato amorfo. Para comparar los beneficios de la capa búfer, se depositó YSZ sobre los tres sustratos mencionados y fueron caracterizados por topografía AFM en cada etapa del crecimiento: Sustratos, capa búfer de YSZ sobre el sustrato, películas de Y-Ba-Cu-O sobre YSZ en cada sustrato y películas de Y-Ba-Cu-O sobre cada uno de los sustratos. Las capas búfer de YSZ y las películas de Y-Ba-Cu-O se depositaron por medio de Rocío Pirolítico Ultrasónico. Las películas crecidas sobre las capas búfer presentan una superficie menos rugosa que aquellas crecidas sobre los sustratos sin capa búfer.

Palabras Claves: Rocío Pirolítico Ultrasónico YbaCuO, YSZ, AFM, rugosidad

1. INTRODUCTION

It is reported that buffer layers benefits the growth of YBCO on substrates that allows diffusion of the species, such as metallic substrates [1-3]. Nevertheless, AFM topographies of spray pyrolysed YBCO films are rarely reported, one reason could be the high roughness of these films.

Stage by stage analysis by AFM technique giving the morphology of the different layers, including the substrate roughness was made to study the growth of these films. Such kinds of analysis were made for other growth techniques and substrates [6-8]. Those techniques are very different from the one used in this research, giving that they are mostly physical deposition techniques, nor chemical ones [1-3, 6, 8, 10-11]

Since the performance of these High Temperature Superconductors (HTSC) is very sensitive to the substrate and the preparation methods employed, in this work we decided to investigate the influence of the substrate and the buffer layer on the morphological aspect of such films.

Nowadays, cubic crystals like magnesium oxide (MgO) and YSZ [4-5,9-12] have been widely used for HTSC thin film coatings applications worldwide.

The influence of precursor was also taken into account, using three different precursors. The buffer layer was studied on every substrate and the same procedure was taken for Y-Ba-Cu-O films.

The principal objective of this work is to show the alternatives of lower cost substrates for YBCO films and the influence of buffer layers to produce these films.

2. EXPERIMENTAL PART

Three different precursor solutions were used:

- Yttrium, Barium and Copper oxides, 0.2 M dissolved in 0.8 M HNO₃ in 14 $\Omega \cdot \text{cm}$ deionised water. Stoichiometric relation Y:Ba:Cu = 1:2:1.
- YBCO powder, 0.03 M in 0.8 M HNO₃ in 14 $\Omega \cdot \text{cm}$ deionised water.
- Yttrium, Barium and Copper nitrates in 14 $\Omega \cdot \text{cm}$ deionised water, with a concentration of 0.2 M and stoichiometric relation Y:Ba:Cu = 1:2:1.

These solutions were calculated to be non-saturated to ensure reproducibility of the experiment, contrary to [13] that used an over-saturated solution to

improve deposition ratio.

The YSZ solution had a concentration of 0.025 M in anhydrous Methanol, using Acetylacetonates of both Yttrium and Zirconium. The experimental setup ,equipment and procedures are the same of [14], reporting YSZ films of cubic and tetragonal atomic structure.

The difference between nitrates solution and oxides solution is the higher pH of the last one. YBCO powder were sintered and proved its superconductivity state, then dissolved to spray them on the films and substrates. The deposition parameters are shown in Table 1. One advantage of using nitrates and oxides solutions is the possibility of making a non-stoichiometric solution to control the deposition ratio of each element to achieve the correct stoichiometry in the films.

All experiments were carried out with and without buffer layer on the three substrates. The substrates were chosen as follows:

- MgO, crystalline with lattice parameters compatible with YBCO.
- Si, Crystalline and incompatible lattice parameters with YBCO.
- SiO₂, Amorphous. There are no good results published with it [4-5].

Polycrystalline films of YSZ have been grown on Silicon and Silica substrates [14], so it might be possible to grow YBCO on those substrates with buffer layers.

Table 1. Deposits parameters

	YSZ	YBCO, 1:2:1Ox, 1:2:1NO ₃
Substrate	450°C	600°C.
Temperature		
Deposition time	20 min	60 min
Transport gas and flux	Air, 3 L / min	Air, 3 L / min
Direction gas and flux	Air, .75 L/min	Air, 0.75 L/min
Annealing	Figure 1	Figure 2

Some profile measurements (Sloan Dektak IIA) and null ellipsometry were carried out to obtain thickness of various YSZ films. AFM topographies and phase imaging were made in AC tapping mode in a JEOL JSPM 4210.

The annealing processes are shown in figures 1 and 2. The figure 1 shows the annealing process for YSZ in a silica tube furnace without special atmosphere of gas. On the other hand, the annealing process made on the Y-Ba-Cu-O films was carried out in the same furnace, with an atmosphere of oxygen exiting by a hose in a flask full of water, pumping two bubbles per minute. These thermal processes are based on the results of [15].

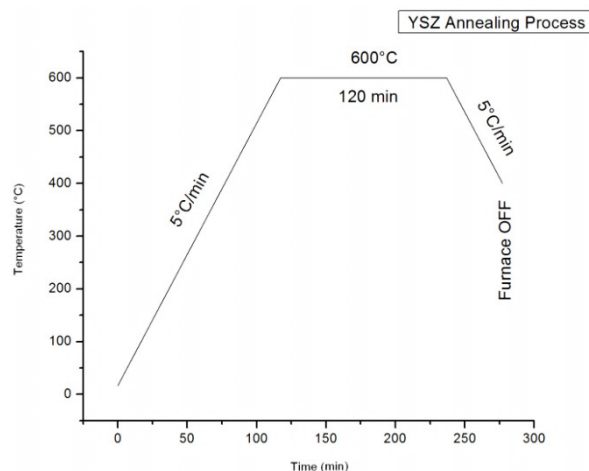


Figure 1. YSZ Annealing Process. The samples are retired from the furnace as they end the annealing.

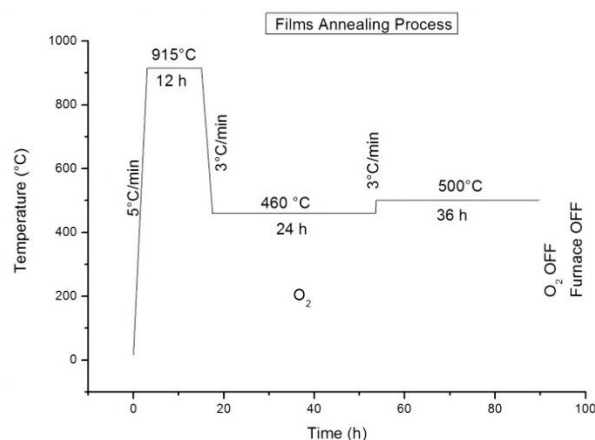


Figure 2. Films Annealing Process. The samples are leaven in the furnace as they end the annealing.

There were eighteen samples in three substrates with and without buffer layer (6 different growth surfaces) and three different precursors. The samples are tagged in reference with their precursor, the presence of buffer layer and the substrate, for example:

a. 1:2:1 Ox/YSZ/MgO refers to the sample grown with oxide precursor solution with buffer layer on

MgO substrate.

b. 1:2:1 NO₃/SiO₂ refers to nitrate precursor solution on bare SiO₂ substrate.

c. YBCO/YSZ/Si refers to YBCO powder solution with buffer layer on Silicon substrate.

All XRD results are similar, showing excess of CuO and Barium oxide deficiency, despite the reduced quantity of Copper oxide in the mixtures of oxides and Nitrates solution. These results are not shown to focus on AFM results and substrate/precursor comparison.

3. RESULTS AND DISCUSSION

Figures 3, 4 and 5 show the growth on the same substrate type, respectively MgO, Si and SiO₂, with Z-scale normalized for direct comparison. Table 3 shows the roughness of the films.

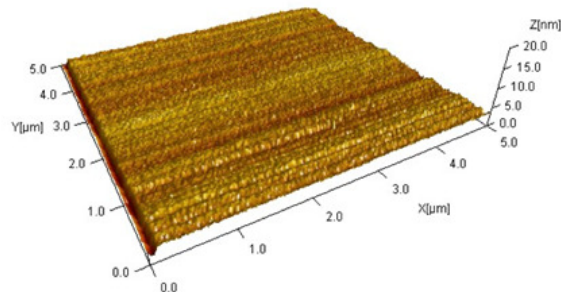
Table 3. Roughness of films (nm)

	MgO	Si	SiO ₂
Substrate	0,2	0,2	0,6
YSZ film	1,2	0,7	2,7
1:2:1 Ox	91,9	68,2	66,2
1:2:1 Ox/YSZ	45,7	67,4	34,2
1:2:1 NO ₃	102,2	170	99,6
1:2:1 NO ₃ /YSZ	85,5	97,3	115,8
YBCO	78,4	161,8	283
YBCO/YSZ	51	65,4	152,3

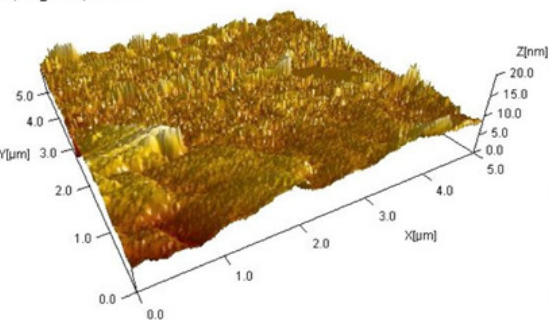
3.1 Films grown on MgO (100):

In Figure 3 a, we can observe that the bare MgO surface exhibits a very regular and flat interface. The RMS roughness value is below the nanometer range. In Figures 3 b,c,d, the films obtained from the deposition of the 3 different precursors onto the bare MgO substrates are shown. The surface morphologies are different in each case. For instance, the 1:2:1 Ox film shows a mixture of granular, peaks and flat terraces areas. When nitrogen was introduced in the precursor material (1:2:1 NO₃), the surface appearance became more regular showing a slab texture with a preferential orientation. Finally, the YBCO film appearance exhibited small and medium size grains grouped in different areas of the substrate. In the last case, it is also possible to observe two small areas where the film coverage is low. In all cases, the RMS values were around 100nm.

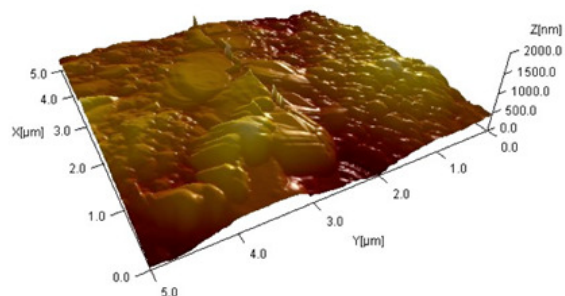
a)
MgO 0,2 nm



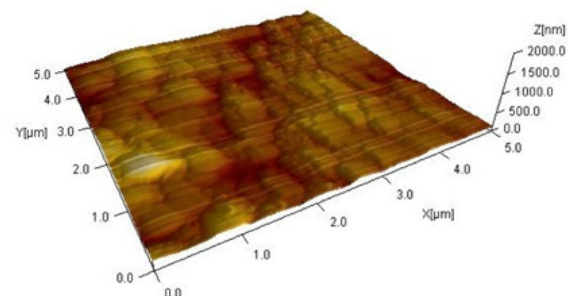
e)
YSZ/MgO 1,2 nm



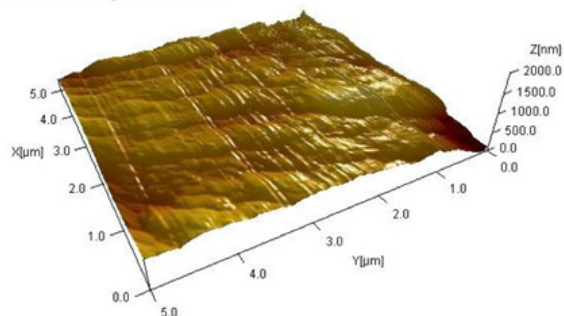
b)
1:2:1Ox/MgO 91,9 nm



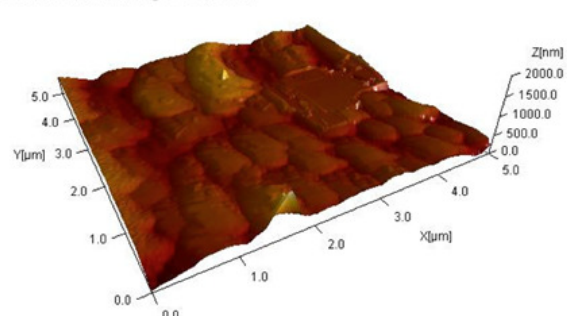
f)
1:2:1Ox/YSZ/MgO 45,7 nm



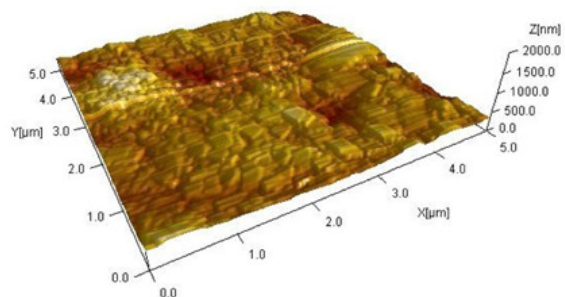
c)
1:2:1NO3/MgO 102,2 nm



g)
1:2:1NO3/YSZ/MgO 85,5 nm



d)
YBCO/MgO 78,4 nm



h)
YBCO/YSZ/MgO 51 nm

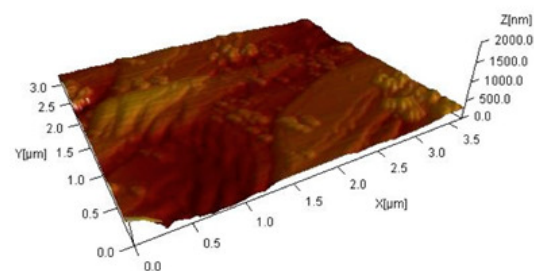
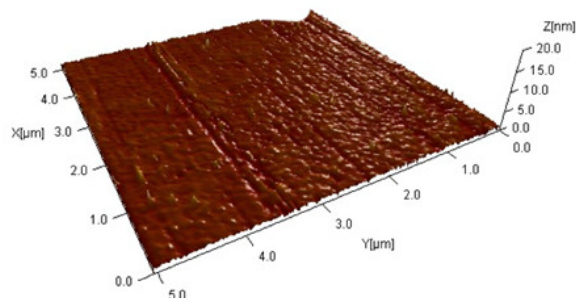


Figure 3. Films deposited onto MgO (100) substrates without (left column) and with (right column) YSZ buffer layers.

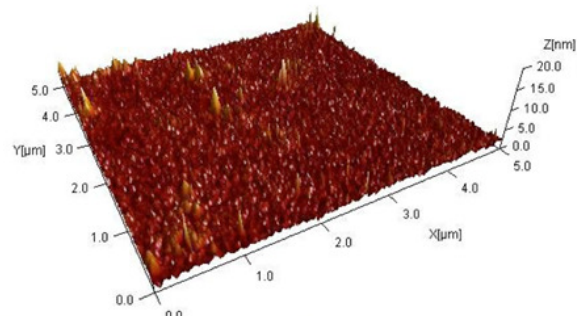
a)

Si 0,2 nm



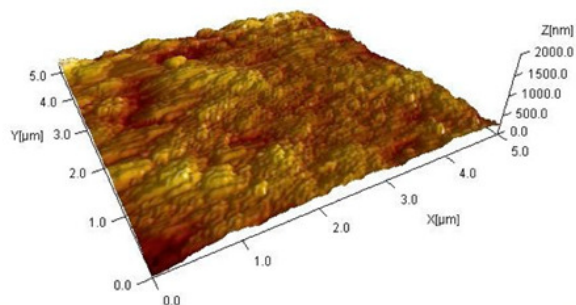
e)

YSZ/Si 0,7 nm



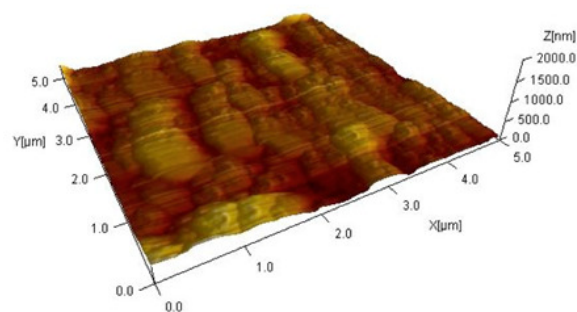
b)

1:2:1Ox/Si 68,2 nm



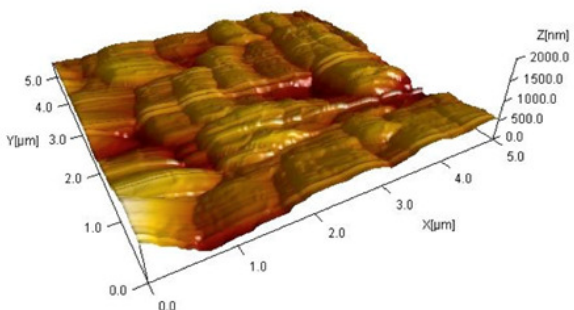
f)

1:2:1Ox/YSZ/Si 67,4 nm



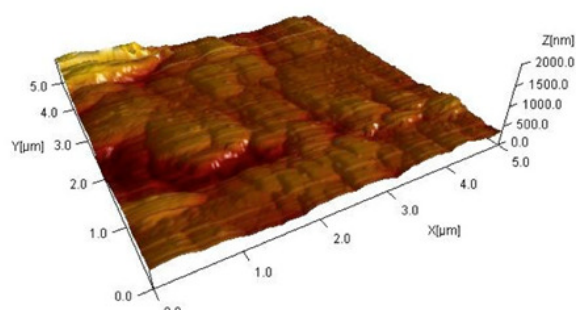
c)

1:2:1NO3/Si 170 nm



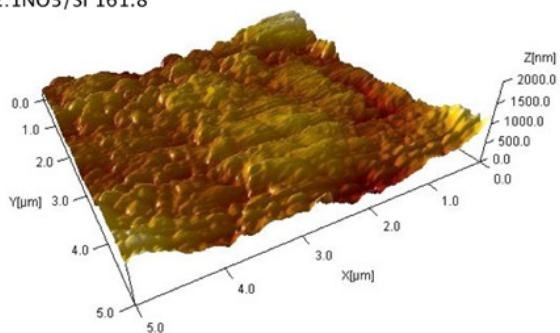
g)

1:2:1NO3/YSZ/Si 97,3 nm



d)

1:2:1NO3/Si 161.8



h)

YBCO/YSZ/Si 65,4 nm

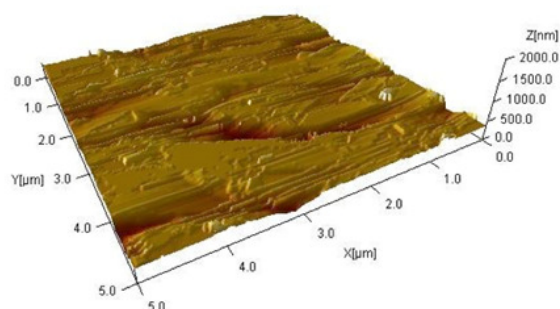


Figure 4. Films deposited on Si (100) substrates without (left column) and with (right column) YSZ buffer layers.

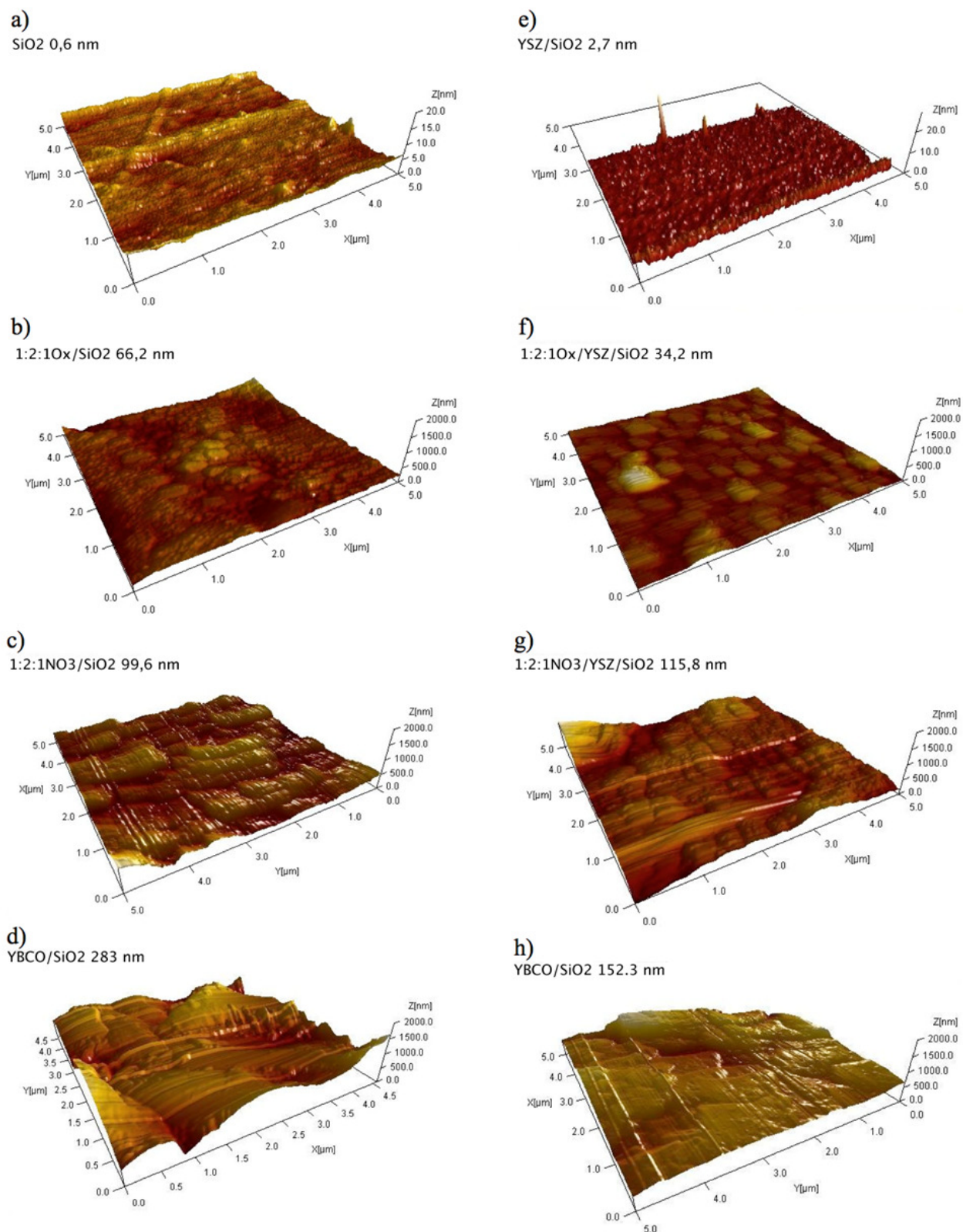


Figure 5. Films deposited on SiO_2 substrates without (left column) and with (right column) YSZ buffer layers.

On the other hand, after the YSZ film was deposited, the surface became irregular in comparison with the bare MgO substrate, although the RMS value remained around 1 nm. This suggests that the deposition technique, as well as the preparation conditions, do not strongly modify the MgO surface roughness after the buffer deposition. When the YBCO films were deposited, the surface texture exhibited step-like features (see Figures 3 f,g). The slab size was smaller for the 1:2:1 Ox film in comparison with the 1:2:1 NO₃ surface, which produced a smoother profile in the first case. Finally, in the YBCO film case, this surface appears to have features much larger than those of the two previous cases with some granular details irregular distributed on the film. This image also shows a large spot where the lack of material is evident. In all cases, the RMS values were below 100nm.

In general, from these images, we can observe that the presence of the YSZ buffer layer improved the final YBCO film texture and reduced considerably the RMS roughness values of films with the same precursor material. On the other hand, the 1:2:1 Ox and the 1:2:1 NO₃ precursors produced smoother films in comparison with the YBCO powder where the surface coverage was uncompleted in both YSZ and bare substrate growths.

3.2 Films grown on Si (100)

The Si (100) used for deposit shows a RMS roughness comparable with MgO substrates, as shown in fig 4 a. Figures 4 b,c,d -the left column- shows the deposition of Y-Ba-Cu-O from different precursors. The morphologies varies abruptly on each one of these precursors, the most different is 1:2:1 Ox / Si figure 4 b) where the roughness is considerably lower than those of nitrates and YBCO powder. Although the roughness of 1:2:1 NO₃ (fig 4 c) is similar to YBCO powder solution (fig 4 d), the surfaces are not the same. Nitrates precursor solution deposits in bigger and coarser grains, overlaying each other, with a preferential orientation. YBCO solution (figure 4 d) deposits in small but coarse grains, with a symmetrical orientation on XY plane. The oxides precursor solution shows the best uniformity and lower roughness.

Once the YSZ buffer films are deposited, Si substrates develop a coarser surface with some peaks distributed in a random way, nevertheless the

roughness is very low (see table 3). YSZ deposited onto this surface changes the behavior of the precursors in the same substrate. First, all the films are smoother than those deposited on bare Si. 1:2:1 Ox/YSZ (figure 4 f) has a very similar roughness with 1:2:1 Ox/Si, but the grains are bigger and highly oriented in Y direction. The morphology of nitrates precursor deposited on YSZ presents smaller grains and lower roughness, there is not overlaying of grains as in the case of nitrates deposited on bare Si and so the uniformity is increased, lowering the roughness. The most particular case is shown in figure 4 h, YBCO/YSZ/Si, where is clear the absence of material and a complete different growth structure: unclear grain structure but certain a smoother surface than YBCO deposited onto bare Si. The best results are obtained for oxides precursor solution in both cases, with and without buffer layer.

3.3 Films grown on SiO₂

Films made on SiO₂ substrates without buffer layer (figures 5 b,c,d) shows uniformity for oxides and nitrates precursor, which are smoother. Oxides precursor solution gives small and oriented grains, meanwhile nitrates solution deposits in bigger but overlaying grains that increases roughness value. Figure 5d shows that the growth of films from YBCO powder solution is difficult, maybe due to the lack of crystallinity of substrate or deposit parameters.

YSZ buffer layer grown on Silica is shown in figure 5 e. The roughness has been increased almost four times, although the appearance of the films is the typical diffractive type of transparent films. Again, the oxide precursor solution gives the lower roughness, also showing homogeneous grain size, uniformly and highly oriented. The slab distribution of the nitrates solution film shows a similarity with the film grown on bare substrate but a higher roughness value produced by the non-uniformity of the deposit process and the in-homogeneity of grain size. Finally, the deposit of YBCO powder solution on non-crystalline substrate was improved with the buffer layer, shown in figure 5 h, this precursor was deposited like slabs containing a few big overlaying grains.

4. CONCLUSIONS

It is clear that YSZ buffer films do not extremely affect the substrate morphologies, as seen on the

AFM obtained roughness values. The amorphous SiO₂ substrate exhibited the higher vertical variations showing that YSZ grows better onto crystalline substrates. This behavior is shown also in the 1:2:1 Ox and YBCO films deposited on buffer layers, where the roughness of SiO₂ substrates is also higher.

The films grown on buffer layers are more homogeneous than those grown on bare substrates, proving that the buffer YSZ layer is convenient to produce smooth Y-Ba-Cu-O films. The roughness is significantly lower by using YSZ buffer layers for all the substrates.

In general, it was observed that the 1:2:1Ox/MgO substrate is more appropriate for Y-Ba-Cu-O growth in contrast with Si and SiO₂. The roughness of grown films onto MgO, are more homogeneous showing roughness values between 45 nm and 102 nm. Nevertheless, although Si substrates show intermediate results, it could be possible to achieve better film qualities by improving the deposition conditions.

Regarding the solution properties, oxides dissolved in aqueous nitric acid gives better results than nitrates dissolved in water, possible due to pH differences, the viscosity and the boiling point values that must be lower in the nitric acid solution. The films deposited with YBCO powder are coarser in contrast with the oxides and nitrates. For industrial applications, these result exhibit important consequences since nitrates and oxides are less expensive in general. Finally, if the difference between these precursors is just the nitric acid presence, it is possible to obtain better results with nitrates by adding nitric acid to that solution instead of using oxide precursors which will decrease the production cost.

Although the results in SiO₂ and Si substrates are not as good as the obtained with MgO substrates, it is possible to grow YBCO on these substrates with the aid of a thicker layer of YSZ, improving the surface for epitaxial growth of these films.

Making a comparison of deposition techniques, we can see that the roughness of the films grown with USP are as smooth as the films grown with more expensive and physical deposition techniques, such as PLD [1,6,8,11], IBAD[2,10] and Magnetron sputtering [3], which are very complex and uses high energy processes, meanwhile Dynamic

Ultrasonic Spray Pyrolysis is a low cost technique and also a simple one. This makes a good option for the growth of such special materials like superconductors.

5. ACKNOWLEDGEMENTS

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