Ultraviolet pulsed laser crystallization of $Ba_{0.8}Sr_{0.2}TiO_3$ films on $LaNiO_3$-coated silicon substrates

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This is the accepted version of the following article:

Queraltó, A.; Pérez Del Pino, A.; De La Mata, M.; [et al.] Ultraviolet pulsed laser crystallization of Ba0.8Sr0.2TiO3 films on LaNiO3-coated silicon substrates. Ceramics International,42(3), 2016. pp 4039-4047,

which has been published in final form at https://doi.org/10.1016/j.ceramint.2015.11.075

ABSTRACT: In this work, $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) films on $LaNiO_3$-buffered SiO_2/Si (LNO/SiO_2/Si) substrates were crystallized by pulsed laser irradiation. Solution-derived amorphous barium-strontium-titanate precursor layers were crystallized with a KrF excimer laser in oxygen ambient at fluences ranging from 50 to 75 mJ cm^{-2}. With the substrate temperature set to 500 ºC, the number of pulses and film thickness were varied until high-quality crystallinity could be achieved. It was found that films with a thickness of 40 nm are fully crystallized with a uniaxial {00l} orientation which is predetermined by the $LaNiO_3$ orientation. On the other hand, for 160 nanometer thick films, crystallization was observed after 12000 pulses in the 70 nm close to the surface, while the rest of the film remained amorphous. The large temperature difference between the film surface and interface due to the low thermal conductivity of the amorphous BST is suggested as the origin of this behavior. Films thicker than 80 nm cracked on crystallization due to the stress caused by the different thermal expansion coefficients of film and substrate, as well as the large temperature variations within the BST film.

KEYWORDS

A. Sol–gel processes; Laser crystallization; D. BaTiO3 and titanates; A. Films

INTRODUCTION

Perovskite oxide films are being explored for numerous functional electronic devices [1-4]. As one example, there is on-going interest in barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$ or BST) for tunable radio-frequency (RF) and microwave components, flexoelectrics, pyroelectrics, and capacitors [4-9]. The dielectric and ferroelectric properties of BST can be tuned through variations in composition, stress, temperature or applied dc electric field [10-13]. Furthermore,

the high dielectric permittivity of BST is suitable for capacitors where high storage densities and low leakage currents are needed [9, 14, 15]. Finally, the high pyroelectric coefficients of BST have also attracted much attention for room temperature infrared detectors and thermal imaging devices [8, 16].

Among the techniques that have been employed to produce BST films [17-19], chemical solution deposition (CSD) is a simple, versatile and low-cost methodology for the development and large-scale implementation of BST films, providing good control over film homogeneity and stoichiometry [10, 20]. Typically, high temperature thermal treatments in conventional furnaces or rapid thermal annealers are used to induce film crystallization. Nevertheless, this methodology cannot be used in applications as wearable electronics which often requires the growth of oxides on temperature sensitive substrates such as polymers. In this sense, photo-irradiation techniques appear as a novel strategy for low-temperature processing due to the photo-induced heating being highly confined in depth [21]. For instance, ultraviolet (UV) lamps have been employed directly or assisting rapid thermal annealing for the crystallization of oxides such as SiO_2, TiO_2 or $PbTiO_3$-based compounds at low temperatures [22-24]. Although UV lamps ensure the growth at temperatures lower than only-thermal treatments, the process is still time consuming requiring tens of minutes to hours of irradiation. In pulsed laser annealing (PLA) of CSD deposited layers, the use of a pulsed source delivers a large amount of energy in a very short time (i.e. nanoseconds) allowing a significantly fast crystallization as recently demonstrated with numerous oxide materials such as epitaxial VO_2, $Ce_{0.9}Zr_{0.1}O_{2-y}$, $Ba_{0.8}Sr_{0.2}TiO_3$ and perovskite manganites (LMO, LSMO) [25-30], or polycrystalline TiO_2, In_2O_3, $Ba_{0.7}Sr_{0.3}TiO_3$ and $(Pb,La)(Zr,Ti)O_3$ [31-34]. Moreover, the spatially-localized heating effect of lasers enables high temperature crystallization of materials such as $BaTiO_3$, silicon or MoS_2 with a minimal

temperature increase on the polymeric substrates below. The resulting materials have good properties and show great potential for the development of flexible electronic devices at large scales [35-37]. PLA can also be readily incorporated into industrial fabrication processes confering this technique a high interest for emerging technologies as macroelectronics. Despite these promising benefits, the use of highly energetic laser sources requires a careful control over different processing parameters to prevent damaging (e.g. amorphization, ablation, etc) the constitutive materials [38]. The precursor film thickness also plays a crucial role in PLA since photo-induced heating is generally highly confined in depth. Thus, the non-homogeneous temperature distribution inside thick film material can provoke its partial crystallization and the development of high thermal stress leading to cracking [33]. In contrast, too thin precursor films or coatings that are transparent to the laser radiation do not develop the needed temperature for initiating crystallization. Therefore, specific photothermal considerations should be taken into account in the design of the treatments.

Laser crystallization of BST deposited by CSD has been reported previously on $Pt/Ti/SiO_2/Si$ substrates [33, 39]. Platinum electrodes have a good electrical conductivity, excellent oxidation resistance, and allow the integration of different oxides with silicon [18, 40]. However, use of $LaNiO_3$ (LNO) enables a cost-effective route for texture control on wide variety of substrates [41]. In this article, an in-depth analysis of the crystallization process of $Ba_{0.8}Sr_{0.2}TiO_3$ films by PLA on $LaNiO_3$ bottom electrodes was performed. The influence of different experimental parameters on crystallization, such as the fluence, number of pulses and film thickness was investigated to develop optimized conditions. Solid-state crystallization was prioritized, in order to avoid melting and resolidification phenomena by using lower fluences. Also, a substrate temperature above room temperature and larger number of pulses were used to decrease

temperature variations between film surface and interface, and to improve film crystallization. Systematic investigations including two-dimensional X-ray diffraction (2D-XRD) were used to further analyze the crystallization process. Numerical simulations based on finite element methods were employed to support the experimental results, providing insight on the thermal evolution of the system and a better appreciation of the photoinduced effects involved during laser crystallization. Finally, efforts were made to evaluate film cracking at high film thicknesses and expand the current understanding about their origin.

MATERIALS AND METHODS

The thin films in this work were prepared using chemical solution deposition (CSD) on oxidized Si wafers. The thickness of the SiO_2 layer was ~1 μm. Firstly, 0.2 M $LaNiO_3$ (LNO) precursor solutions, prepared as described in ref [27], were deposited by spin-coating at 6000 rpm for 2 min on thoroughly cleaned 4-inch SiO_2/Si wafers (NOVA Electronic Materials, LLC). Each layer was pyrolyzed at 350 ºC for 10 min on a hot-plate and crystallized at 700 ºC for 1 min, with a heating ramp of 20 ºC s^{-1} in oxygen ambient using a rapid thermal annealer (RTP-600S, Modular Process Technology Corp.). Four repetitions were needed to reach a thickness of ~150 nm. The final LNO films had a root mean square (RMS) roughness of ~0.8 nm, and some uniaxial texture with the (00l) orientation as shown in the Supporting Information (Figures S1 and S2). In particular, LNO buffer layers have a uniaxial fraction of 61±8 %. The LNO-coated wafers were cut into pieces of approximately 5×5 mm^2.

Stoichiometric $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) precursor solutions with a 0.3 M concentration were prepared as described elsewhere [27]. These solutions were spun onto the $LaNiO_3$-coated

substrate using the same conditions as for the $LaNiO_3$, and were fully decomposed at 450 ºC for 10 min on a hot-plate after each coating. The thickness of the amorphous pyrolyzed film was varied between 40 and 160 nm by repeating the deposition and pyrolysis steps.

Pulsed laser annealing of the BST films was carried out using a KrF excimer laser (COMPex Pro 102, Coherent Inc.) working at 248 nm with pulses of 20 ns in duration and a repetition rate of 20 Hz. The energy density at the film surface was controlled by adjusting the incoming laser energy, and varying the spot size with a plano-convex lens. Films were irradiated inside a vacuum chamber brought down to a residual pressure of 10^{-7} Torr, which was then filled with pure oxygen at a pressure of 0.1 Torr. Samples were mounted on a substrate heater using silver paint. The substrate temperature was controlled within ±3 ºC by employing a Eurotherm Digital Temperature Controller 847.

The morphological characterization of film surfaces was conducted using an Agilent 5100 atomic force microscope (AFM) and a FEI NanoSEM 630 scanning electron microscope (SEM). The micrographs were analyzed with the MountainsMap 7.0 software (Digital Surf). The crystallographic structure of the films was measured by X-ray diffraction (XRD) using a Cu-Kα radiation source with a PANalytical X'Pert Pro MPD diffractometer and a Bruker GADDS system equipped with a 2-dimensional detector. More detailed analysis of the film crystallization was attained by means of high resolution transmission electron microscopy (HRTEM) of cross-sectional specimens produced by mechanical polishing and ion milling. The HRTEM images were acquired with FEI Tecnai F20 and JEOL J2010F microscopes both equipped with field-emission guns working at 200 kV and achieving lateral resolutions of 0.14 nm. Electron energy loss spectroscopy (EELS) analyses were conducted in a FEI Tecnai F20 and FEI Titan S/TEM both equipped with post-column Gatan Image Filter energy spectrometers.

Finally, the laser-induced thermal behaviour in the samples were simulated by solving the transient heat equation with the finite element method by employing COMSOL 4.4 Multiphysics software [26]. Additional information on simulations can be found in the supporting information. The optical and thermophysical properties of films and substrate used in the calculations were reported in refs [21, 27, 42-45] and are summarized in the Supporting Information (Table S1).

RESULTS AND DISCUSSION

1. Study at different fluences and number of pulses

Numerical simulations were used to estimate appropriate irradiation conditions. The amount of radiation absorbed is characterized by the optical absorption coefficient, α, as described by the Beer-Lambert law. In particular, amorphous BST has an optical absorption coefficient α_{BST} at λ=248 nm of 28.1×10^6 m^{-1} [27], which corresponds to an optical penetration length of l_α^{BST}~36 nm. Thus, a film with a thickness of 40 nm will absorb about a 68% of the incoming radiation, and the remaining intensity will be absorbed through the 150 nm thick LNO buffer layer ($\alpha_{LNO}=23.6\times10^6$ m^{-1} and l_α^{LNO}~42 nm at λ=248 nm) [27].

It can be assumed that the amorphous BST film is mostly composed of Ba-O, Sr-O and Ti-O bonds with dissociation energies between 454 and 662 kJ mol^{-1} (4.7 and 6.9 eV/bond) [46], whereas the laser photon energy is ~5 eV at 248 nm. Two major phenomena can be induced upon absorption of the laser radiation, i.e. photochemical and photothermal interactions. Photochemical mechanisms associated with the direct dissociation of chemical bonds may occur given that the laser photon energy is slightly higher than the lower limit for bond dissociation

energies. However, photothermal effects have been reported to be predominant for nanosecond-pulsed lasers [21]. Thus, for the sake of simplicity, it has been assumed that the interaction between laser radiation and films is essentially photothermal. The film pyrolysis procedure followed in the experimental section ensured the elimination of organic residues as reported for other propionate derived films within a detection limit of approximately 0.8 wt% [47, 48]. If any C-C, C-O and C-H bonds remained, they would be photochemically decomposed during initial stages of irradiation since their energies are significantly lower than the laser photon energy (3.6-4.3 eV/bond) [48].

Figure 1a shows the temperature profiles obtained from photothermal simulations of 40 nanometer thick BST films on LNO/SiO_2/Si substrates for fluences of 50, 65 and 75 mJ cm^{-2}, a substrate temperature of 500 ºC and a single laser pulse. The chosen conditions allow similar maximum temperatures to the ones reported in ref [27], i.e. between ~1100-1450 ºC. According to simulations, laser pulses provoke rapid thermal cycles without exceeding the melting point of the system constituents - (Supporting Information, Table S1). The high temperatures induced lead to heating/cooling rates up to 10^9 ºC s^{-1}. The temperature profiles developed in the BST film last from hundreds to thousands of nanoseconds. As a result, large temperature differences are induced between the film surface and the BST/LNO interface. These variations lead to maximum temperature gradients inside the film of 10^8-10^9 ºC m^{-1} during tens of nanoseconds. Additionally, the effective heating time for a single pulse t_{eff} (here defined as the time the film is above 600 ºC, which is used as the minimum temperature needed for BST crystallization [49]) can be extracted. In particular, it can be seen that t_{eff} increases with the fluence from approximately 0.8 (50 mJ cm^{-2}) to 1.1 μs (75 mJ cm^{-2}). It is also important to highlight that these values of effective heating time are one to two orders of magnitude longer than those reported elsewhere [26, 27, 39, 50].

These differences mainly arise due to the different laser systems employed, experimental conditions (fluence and substrate temperature) and thermophysical parameters of the constituent materials.

Laser irradiation of amorphous BST (after the pyrolysis of the precursors) on LNO/SiO_2/Si was performed at fluences of 50, 65 and 75 mJ cm^{-2}; samples were irradiated with 12000 pulses while held at a substrate temperature of 500 ºC. XRD diffractograms in Figure 1b show the peaks corresponding to the silicon substrate and LNO buffer layer. Also, the BST (001) and (002) peaks are identified at ~22.2º and ~45.4º, respectively, and the polycrystalline BST (011) reflection is found at ~31.7º. No crystallization of BST is detected at 50 mJ cm^{-2}, whereas BST peaks are observed at 65 and 75 mJ cm^{-2}. These results indicate that the temperature reached at 50 mJ cm^{-2} (Figure 1a) may be insufficient to promote crystallization for the very short laser annealing times employed. Thus, either higher fluences or larger number of pulses should be used.

Figure 2 shows the percentage of {100} texture fraction for BST films with thicknesses of 40 and 160 nm, fluences of 65 and 75 mJ cm^{-2}, and number of pulses between 1200 and 72000, as indicated. The methodology used (Supporting Information) is an improvement from semi-quantitative methods like the Lotgering factor [51]. The values for 40 nm-thick BST samples treated at 65 and 75 mJ cm^{-2} after 12000 pulses (substrate at 500 ºC) obtained from the Lotgering factor method would have been 0.63±0.03 and 0.77±0.04, respectively. In contrast, the proposed quantification methodology shows uniaxial fractions of 21±7 % and 26±5 %, respectively. Therefore, these films essentially have a random orientation although some degree of texture is detected along the {00l} orientation, which seems to increase slightly with the laser fluence. The same method has been previously employed to evaluate the epitaxial content of ceria thin films

produced by laser annealing, giving epitaxial fraction values close to 100 % [26]. The surface morphology of films irradiated at 50 and 65 mJ cm^{-2} as shown in Figures 1c and d, reveals granular and porous surfaces. Furthermore, grains with tens of nanometers in size are also seen, which led to RMS roughnesses of 3.0 and 5.2 nm, respectively. The sample irradiated at 75 mJ cm^{-2} (Figure 1e) has a RMS roughness of 8.3 nm and displays larger groups of grains with sizes of hundreds of nanometers. Moreover, the grains are separated by boundaries that could be associated with grain boundary grooving, similar to those reported in ref [26].

A fluence of 65 mJ cm^{-2} was selected for a substrate temperature of 500 ºC since those conditions allow laser crystallization of BST with a rather homogeneous surface with low roughness. To investigate how the film surface morphology and crystallization is affected, the number of laser pulses was varied between 1200 and 72000 pulses. After accumulating 1200 pulses (Figure 3a), the surface shows two sets of features, one with compact grains smaller than 100 nm and the other larger than ~300 nm. The RMS roughness of the film is ~3.5 nm. The larger features could be associated with residual amorphous material, as they seem to disappear as the number of pulses increases to 12000 and 72000 (Figures 1d and 3b). The RMS roughness increased to 5.2 and 6.9 nm, respectively, because the smaller grains enlarge and the surface morphology becomes porous as mentioned earlier. XRD analyses of films irradiated for 1200, 12000 and 72000 pulses (Figure 3c) illustrate the presence of (00l) and (011) orientations of BST, as reported previously. Based on the increase in the BST (002) peak area, the degree of crystallization increases with the number of pulses. Presumably, this is caused by the longer cumulative heating time achieved at higher number of pulses as it has been reported for other oxide films on different substrate architectures [26, 27, 33, 50]. Accordingly, longer heating times would allow the film constituents to rearrange into the final phase and also form larger

crystallites through grain coarsening, which should lead to sharper and more intense XRD peaks. The 2D-XRD pattern of a film irradiated at 65 mJ cm^{-2}, a substrate temperature of 500 ºC and 72000 pulses (Figure 3d) reveals that the BST film has some {00l} oriented material, as evidenced by the higher peak intensity for values close to χ=0º (depicted with a dashed white line). The percentages of {100} orientation for films irradiated with 1200, 12000 and 72000 pulses at 65 mJ cm^{-2} are 13±5 %, 21±7 % and 35±6 %, respectively, as shown in Figure 2. The degree of orientation increases with the number of pulses, suggesting that the BST is trying to mimic the (001) texture of the LNO buffer layer (uniaxial fraction of 61±8 %) as more pulses are applied.

2. Effect of film thickness on crystallization

Usually, the strategy followed for the fabrication of BST devices from chemical solutions is based on the deposition of multiple coatings until the desired thickness is reached [4, 13, 16]. In this section, laser crystallization of films with thicknesses between 40 and 160 nm is described. The methodology followed to obtain thicker films is based on several deposition and pyrolysis steps, as described in the experimental section.

SEM analyses in Figures 4a and b illustrate the resulting surface morphologies for films (laser annealed at 65 mJ cm^{-2} with a substrate temperature of 500ºC for 72000 pulses). It was found that the sample with a thickness of 40 nm is homogeneous with grains/pores of 100 nm in size and a RMS roughness of 6.9 nm, as already described. On the other hand, the film with a thickness of 160 nm presents a heterogeneous surface with lateral grain sizes exceeding 1 μm, resulting in a RMS roughness of 18.9 nm. Cracks also appear. Figure 4c depicts the XRD

measurements of BST films with thicknesses of 40 and 160 nm. Particularly, the θ-2θ scans reveal the increasing intensity of the BST reflections with the film thickness because of the larger sampled volume. The uniaxial fraction values for films with thicknesses of 40 and 160 nm and irradiated at 65 mJ cm^{-2} and 72000 pulses are 35±6 % and 29±7 %, respectively, revealing the presence of a large amount of polycrystalline material in the films.

HRTEM investigations of BST films after laser treatment at 65 mJ cm^{-2} for 12000 pulses at a substrate temperature of 500ºC were conducted. Figures 5a and b show a STEM image (performed under Annular Dark Field, ADF, conditions) and the corresponding intensity profile of the sample. The 40 nanometer thick BST film can be identified along with the LNO multilayered film and the amorphous SiO_2 layer. Figure 5b depicts an HRTEM image and power spectrum (fast Fourier transform, FFT) of a zoomed area into the square in Figure 5a, showing two different BST grains with different in-plane orientations. In contrast, Figure 5c shows the TEM characterization of a ~160 nm thick BST film, depicting a partially crystallized layer. More precisely, Figures 5d and e show a ~70 nanometer thick region close to the surface comprised of polycrystalline (randomly oriented) material, whereas the remaining film closer to the interface with the LNO (Figure 5f) is amorphous. The percentage of uniaxial fraction in this sample is around 15-30 % (Figure 2).

The transfer of texture from the LNO layer seems improbable provided nucleation is induced from their surface. Despite that, the homogeneity of this crystalline/amorphous layer cannot be completely evaluated due to the local nature of TEM. Thus, thicker films could present areas with a tendency to crystallize down to the interface, while other regions may have amorphous regions like the one depicted in Figure 5f. In addition, *ab initio* calculations of the surface energies for $BaTiO_3$ indicate that a lower energy is required to form a {00l} oriented surface [52,

53]. Therefore, it could also be more favorable thermodynamically to form grains with a {00l} orientation. The differences observed between the two samples can be explained in terms of the absorbed radiation intensity, which is higher at the surface and decays exponentially inside the film as described by the Beer-Lambert law. As mentioned before, the heating process depends to a great extent on the optical penetration depth l_α of each material. It should be remembered that 68% of the incoming radiation is absorbed through the 40 nanometer BST film (l_α^{BST}~36 nm at λ~248 nm). The rest of the radiation is transmitted to (and absorbed in) the LNO buffer layer. In contrast, the laser radiation is completely absorbed in the 160 nanometer thick BST layer. As a result, the temperature profiles extracted from simulations for 40 and 160 nanometer thick BST films on LNO/SiO_2/Si substrates (Figure 6a) reveal comparable temperature profiles at the film surface. However, there is a large difference in the temperature reached at the interface with LNO, i.e. the surface-interface temperature differences are around 50 and 300 ºC for 40 and 160 nm thick films, respectively. These results are similar to those reported previously [39, 50]. It is notable that the interface temperature for the 160 nm film, around 1000 ºC, may be insufficient to promote the laser crystallization for a limited number of short pulses (Figure 5c). These results are in agreement with previous observations for 40 nanometer films where it was shown that crystallization is not detected for laser fluences as low as 50 mJ cm^{-2} (equivalent to temperatures of ~1100 ºC).

Cracks were observed in 160 nm thick films after being irradiated at 65 mJ cm^{-2} for 72000 pulses at a substrate temperature of 500 ºC. Comparable reports of the presence of cracks for laser-crystallized BST films on Pt/SiO_2/Si substrates have been given elsewhere [33, 39]. Specifically, it was determined that cracks appeared for thicknesses above 130 nm, even for laser energy densities as low as 50 mJ cm^{-2}. In the same way, in this work, cracking was observed for films

with thicknesses of ~160 nm even after laser annealing at 50 mJ cm^{-2}, 72000 pulses and a substrate temperature of 500 ºC (Figure S4). No cracks could be observed for a thickness of 80 nm. Film cracking is a form of stress relaxation that occurs when elastic energy accumulates in the film until it exceeds a critical value. There are several physical mechanisms that lead to stress accumulation and crack formation. First, we considered the thermal stress derived from different thermal expansion coefficients (TECs) of the materials forming the system. The respective TECs of BST and LNO are approximately 12.9×10^{-6} K^{-1} and 8.2×10^{-6} K^{-1} [54, 55], and even a larger difference is attained between these values and the thermal expansion coefficient of SiO_2 (0.5×10^{-6} K^{-1} [56]), which will certainly lead to stress development in the system. Temperature simulations in Figure 6b indicate that the silicon (1.4×10^{-6} K^{-1} [55]) is at the initial substrate temperature.

Because of its thickness, it is expected to impose stress on the whole BST/LNO/SiO_2/Si structure. Also, there is the large temperature gradients associated laser heating/cooling. Simulations in Figure 6 show a temperature variation of ~300ºC between the surface and interface for 160 nanometer thick BST films giving rise to a temperature gradient of $\sim2\times10^{9}$ ºC m^{-1}. This film cracks. However, the temperature gradient is reduced down to $1x10^{9}$ ºC m^{-1} for the 40 nm films, which did not crack. Therefore, the film thickness seems to be a critical parameter controlling crack formation in the current system as stress builds up with the increase in thickness. Finally, it is important to note that different degrees of crystallization exist between the surface and interface in thick films, i.e. the film is polycrystalline at the surface and still amorphous at the interface (Figure 5c-f). Thus, stress may be generated during film growth related to the densification process occurring during the transformation from amorphous to crystalline material, as reported previously [33]. The stress caused by lattice mismatch is

irrelevant here since there is no epitaxial growth. The results provided here would suggest that either films with thicknesses below 160 nm should be grown or, instead, a strategy with consecutive pyrolysis and crystallization steps should be followed until the desired thickness is reached. This should prevent excessively large temperature differences and film densification, hence diminishing the development of cracks.

CONCLUSIONS

Solution-derived amorphous BST films were crystallized on LNO-coated silicon wafers at low substrate temperatures mainly due to photothermal interactions derived from the absorption of laser radiation. The experimental conditions lead to a solid state crystallization, i.e. the maximum simulated temperatures in the BST layer are below the melting point. The films have a certain degree of uniaxial {00l} crystalline texture that could be attributed to the lower surface energy needed to form these grains, as well as the presence of some crystalline regions that reach the interface in thicker films. Moreover, the amount of crystalline material increased with the fluence and number of pulses since higher temperatures and longer cumulative annealing times are developed in the system. Temperature simulations point toward cumulative effective heating times in the range of milliseconds. Careful control of the thickness is mandatory since it has also been found to affect the crystallinity. In particular, layers with a thickness of 40 nm are fully crystallized, while only a ~70 nm depth near the surface is crystallized in 160 nanometer thick films. Temperature inhomogeneity through the thickness coupled with the very short effective heating times of the laser treatments are proposed as the main sources for partially crystallized layers. Additionally, these phenomena together with the different thermal expansion coefficients

of materials and film thickness can generate stress in the system that result in the formation of cracks. Consequently, careful control of the processing parameters must be done to prevent noncrystallized areas and crack formation from hindering the functionality of the films.

ACKNOWLEDGEMENTS

This work was financed by the Ministry of Economy and Competitiveness under the projects MAT2011-28874-C02-01, MAT2014-51778-C2-1-R, ENE2014-56109-C3-3-R and Consolider Nanoselect CSD2007-00041, and by Generalitat de Catalunya (2015 SGR 753 and Xarmae). AQ and MdlM are also grateful for JAE-Predoc fellowship and European Social Fund program. Fruitful discussions with Dr. Susagna Ricart for solution synthesis are also acknowledged.

SUPPLEMENTARY MATERIAL

AFM and XRD characterization of LNO/SiO_2/Si substrates, description of the quantitative method for the evaluation of film texture from 2D-XRD, description of the numerical model used for photothermal simulations, thermophysical and optical parameters of BST, LNO, SiO_2 and Si, in SC and YSZ/SS, SEM characterization of BST films irradiated at 50 mJ cm^{-2} and 500ºC of substrate temperature and a thickness of 80 nm.

REFERENCES

[1] A. Kingon, Perovskites: Is the ultimate memory in sight?, Nat Mater, 5 (2006) 251-252.

[2] J.F. Scott, Applications of Modern Ferroelectrics, Science, 315 (2007) 954-959.
[3] M.G. Blamire, J.L. MacManus-Driscoll, N.D. Mathur, Z.H. Barber, The materials science of functional oxide thin films, Advanced Materials, 21 (2009) 3827-3839.
[4] N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N.Y. Park, G.B. Stephenson, I. Stolitchnov, A.K. Taganstev, D.V. Taylor, T. Yamada, S. Streiffer, Ferroelectric thin films: Review of materials, properties, and applications, J. Appl. Phys., 100 (2006) 051606-051646.
[5] S.W. Kirchoefer, E.J. Cukauskas, N.S. Barker, H.S. Newman, W. Chang, Barium–strontium–titanate thin films for application in radio-frequency-microelectromechanical capacitive switches, Applied Physics Letters, 80 (2002) 1255-1257.
[6] A. Tombak, J.P. Maria, F. Ayguavives, G.T. Stauf, A.I. Kingon, A. Mortazawi, Tunable barium strontium titanate thin film capacitors for RF and microwave applications, IEEE Microwave and Wireless Components Letters, 12 (2002) 3-5.
[7] S.R. Kwon, W. Huang, L. Shu, F.-G. Yuan, J.-P. Maria, X. Jiang, Flexoelectricity in barium strontium titanate thin film, Applied Physics Letters, 105 (2014) 142904.
[8] T. Zhang, H. Ni, Pyroelectric and dielectric properties of sol–gel derived barium–strontium–titanate ($Ba_{0.64}Sr_{0.36}TiO_3$) thin films, Sensors and Actuators A: Physical, 100 (2002) 252-256.
[9] K. Kageyama, T. Hosokura, T. Nakaiso, H. Takagi, Dielectric properties of (Ba,Sr)TiO_3 thin films with varied microstructures prepared by the chemical solution deposition method for thin-film capacitors and ferroelectric varactors, Ultrasonics, Ferroelectrics, and Frequency Control, IEEE Transactions on, 57 (2010) 2198-2204.
[10] D. Levasseur, H.B. El-Shaarawi, S. Pacchini, A. Rousseau, S. Payan, G. Guegan, M. Maglione, Systematic investigation of the annealing temperature and composition effects on the dielectric properties of sol–gel $Ba_xSr_{1-x}TiO_3$ thin films, Journal of the European Ceramic Society, 33 (2013) 139-146.
[11] T.M. Shaw, Z. Suo, M. Huang, E. Liniger, R.B. Laibowitz, J.D. Baniecki, The effect of stress on the dielectric properties of barium strontium titanate thin films, Applied Physics Letters, 75 (1999) 2129-2131.
[12] C. Basceri, S.K. Streiffer, A.I. Kingon, R. Waser, The dielectric response as a function of temperature and film thickness of fiber-textured (Ba,Sr)TiO_3 thin films grown by chemical vapor deposition, J. Appl. Phys., 82 (1997) 2497-2504.
[13] L.M. Garten, P. Lam, D. Harris, J.-P. Maria, S. Trolier-McKinstry, Residual ferroelectricity in barium strontium titanate thin film tunable dielectrics, J. Appl. Phys., 116 (2014) 044104.
[14] A.I. Kingon, S.K. Streiffer, C. Basceri, S.R. Summerfelt, High-Permittivity Perovskite Thin Films for Dynamic Random-Access Memories, MRS Bulletin, 21 (1996) 46-52.
[15] G.W. Dietz, M. Schumacher, R. Waser, S.K. Streiffer, C. Basceri, A.I. Kingon, Leakage currents in $Ba_{0.7}Sr_{0.3}TiO_3$ thin films for ultrahigh-density dynamic random access memories, J. Appl. Phys., 82 (1997) 2359-2364.
[16] J.-G. Cheng, J. Tang, J.-H. Chu, A.-J. Zhang, Pyroelectric properties in sol–gel derived barium strontium titanate thin films using a highly diluted precursor solution, Applied Physics Letters, 77 (2000) 1035-1037.
[17] C.S. Hwang, S.O. Park, H.J. Cho, C.S. Kang, H.K. Kang, S.I. Lee, M.Y. Lee, Deposition of extremely thin (Ba,Sr)TiO_3 thin films for ultra-large-scale integrated dynamic random access memory application, Applied Physics Letters, 67 (1995) 2819-2821.

[18] L. Goux, M. Gervais, A. Catherinot, C. Champeaux, F. Sabary, Crystalline and electrical properties of pulsed laser deposited BST on platinized silicon substrates, Journal of Non-Crystalline Solids, 303 (2002) 194-200.
[19] S. Regnery, Y. Ding, P. Ehrhart, C.L. Jia, K. Szot, R. Thomas, R. Waser, Metal-organic chemical-vapor deposition of (Ba,Sr)TiO_3: Nucleation and growth on Pt-(111), J. Appl. Phys., 98 (2005) 084904.
[20] M.C. Gust, L.A. Momoda, N.D. Evans, M.L. Mecartney, Crystallization of Sol-Gel-Derived Barium Strontium Titanate Thin Films, J Am Ceram Soc, 84 (2001) 1087-1092.
[21] D. Bäuerle, Laser processing and chemistry, Springer, 2011.
[22] H. Imai, M. Yasumori, H. Hirashima, K. Awazu, H. Onuki, Significant densification of sol-gel derived amorphous silica films by vacuum ultraviolet irradiation, J. Appl. Phys., 79 (1996) 8304-8309.
[23] R.E. Van de Leest, UV photo-annealing of thin sol-gel films, Applied Surface Science, 86 (1995) 278-285.
[24] M.L. Calzada, I. Bretos, R. Jiménez, H. Guillon, L. Pardo, Low-Temperature Processing of Ferroelectric Thin Films Compatible with Silicon Integrated Circuit Technology, Advanced Materials, 16 (2004) 1620-1624.
[25] M. Nishikawa, T. Nakajima, T. Kumagai, T. Okutani, T. Tsuchiya, Photoassisted chemical solution deposition method for fabricating uniformly epitaxial VO_2 films, Applied Physics A: Materials Science & Processing, 100 (2010) 297-303.
[26] A. Queraltó, Á. Pérez del Pino, M. de la Mata, J. Arbiol, X. Obradors, T. Puig, Ultrafast crystallization of $Ce_{0.9}Zr_{0.1}O_{2-y}$ epitaxial films on flexible technical substrates by pulsed laser irradiation of chemical solution derived precursor layers, Crystal Growth & Design, 15 (2015) 1957-1967.
[27] A. Queraltó, A. Pérez del Pino, M. de la Mata, J. Arbiol, M. Tristany, A. Gómez, X. Obradors, T. Puig, Growth of ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ epitaxial films by ultraviolet pulsed laser irradiation of chemical solution derived precursor layers, Applied Physics Letters, 106 (2015) 262903.
[28] T. Nakajima, T. Tsuchiya, M. Ichihara, H. Nagai, T. Kumagai, Epitaxial Growth Mechanism for Perovskite Oxide Thin Films under Pulsed Laser Irradiation in Chemical Solution Deposition Process, Chemistry of Materials, 20 (2008) 7344-7351.
[29] T. Tsuchiya, T. Nakajima, T. Kumagai, Influence of the laser wavelength on the epitaxial growth and electrical properties of $La_{0.8}Sr_{0.2}MnO_3$ films grown by excimer laser-assisted MOD, Applied Surface Science, 255 (2009) 9804-9807.
[30] T. Nakajima, K. Shinoda, T. Tsuchiya, UV-assisted nucleation and growth of oxide films from chemical solutions, Chemical Society Reviews, 43 (2014) 2027-2041.
[31] E.S. Ghaith, T. Hayakawa, T. Kasuga, M. Nogami, Apatite formation on rutile type TiO_2 films formed by laser irradiation, J Mater Sci, 41 (2006) 2521-2524.
[32] H. Imai, A. Tominaga, H. Hirashima, M. Toki, M. Aizawa, Ultraviolet-laser-induced crystallization of sol-gel derived indium oxide films, J Sol-Gel Sci Technol, 13 (1998) 991-994.
[33] O. Baldus, R. Waser, Laser crystallization studies of barium strontium titanate thin films, Journal of the European Ceramic Society, 24 (2004) 3013-3020.
[34] S.S.N. Bharadwaja, T. Dechakupt, S. Trolier-McKinstry, H. Beratan, Excimer laser crystallized (Pb,La)(Zr,Ti)O_3 thin films, J Am Ceram Soc, 91 (2008) 1580-1585.

[35] E.D. Tsagarakis, C. Lew, M.O. Thompson, E.P. Giannelis, Nanocrystalline barium titanate films on flexible plastic substrates via pulsed laser annealing, Applied Physics Letters, 89 (2006) 202910.
[36] T. Pier, K. Kandoussi, C. Simon, N. Coulon, T. Mohammed-Brahim, H. Lhermite, Excimer laser crystallization of microcrystalline silicon for TFTs on flexible substrate, Journal of Non-Crystalline Solids, 354 (2008) 2300-2304.
[37] H. Kwon, W. Choi, D. Lee, Y. Lee, J. Kwon, B. Yoo, C. Grigoropoulos, S. Kim, Selective and localized laser annealing effect for high-performance flexible multilayer MoS_2 thin-film transistors, Nano Res., 7 (2014) 1137-1145.
[38] N. Asakuma, T. Fukui, M. Toki, H. Imai, Low-temperature synthesis of ITO thin films using an ultraviolet laser for conductive coating on organic polymer substrates, J Sol-Gel Sci Technol, 27 (2003) 91-95.
[39] S. Halder, U. Boettger, T. Schneller, R. Waser, O. Baldus, P. Jacobs, M. Wehner, Laser annealing of BST thin films with reduced cracking at an elevated temperature, Materials Science and Engineering: B, 133 (2006) 235-240.
[40] G.R. Fox, S. Trolier-McKinstry, S.B. Krupanidhi, L.M. Casas, Pt/Ti/SiO_2/Si substrates, Journal of Materials Research, 10 (1995) 1508-1515.
[41] D. Bao, N. Wakiya, K. Shinozaki, N. Mizutani, X. Yao, Improved electrical properties of (Pb,La)TiO_3 thin films using compositionally and structurally compatible $LaNiO_3$ thin films as bottom electrodes, Applied Physics Letters, 78 (2001) 3286-3288.
[42] J. Mistrik, T. Yamaguchi, D. Franta, I. Ohlidal, G.J. Hu, N. Dai, Optical properties of rough $LaNiO_3$ thin films studied by spectroscopic ellipsometry and reflectometry, Applied Surface Science, 244 (2005) 431-434.
[43] S.C. Lai, H.T. Lue, K.Y. Hsieh, S.L. Lung, R. Liu, T.B. Wu, P.P. Donohue, P. Rumsby, Extended-pulse excimer laser annealing of Pb($Zr_{1-x}Ti_x$)O_3 thin film on $LaNiO_3$ electrode, J. Appl. Phys., 96 (2004) 2779-2784.
[44] M. Zinkevich, F. Aldinger, Thermodynamic analysis of the ternary La-Ni-O system, J Alloy Compd, 375 (2004) 147-161.
[45] S.T. Davitadze, S.N. Kravchun, B.A. Strukov, B.M. Goltzman, V.V. Lemanov, S.G. Shulman, Specific heat and thermal conductivity of $BaTiO_3$ polycrystalline thin films, Applied Physics Letters, 80 (2002) 1631-1633.
[46] J. Speight, Lange's handbook of chemistry, McGraw-Hill, New York, 2005.
[47] P. Roura, J. Farjas, S. Ricart, M. Aklalouch, R. Guzman, J. Arbiol, T. Puig, A. Calleja, O. Peña-Rodríguez, M. Garriga, X. Obradors, Synthesis of nanocrystalline ceria thin films by low-temperature thermal decomposition of Ce-propionate, Thin Solid Films, 520 (2012) 1949-1953.
[48] A. Queraltó, Á. Pérez del Pino, S. Ricart, X. Obradors, T. Puig, Laser-induced metal organic decomposition for $Ce_{0.9}Zr_{0.1}O_{2-y}$ epitaxial thin film growth, J Alloy Compd, 574 (2013) 246-254.
[49] U. Hasenkox, S. Hoffmann, R. Waser, Influence of Precursor Chemistry on the Formation of $MTiO_3$ (M = Ba, Sr) Ceramic Thin Films, J Sol-Gel Sci Technol, 12 (1998) 67-79.
[50] S.S.N. Bharadwaja, J. Kulik, R. Akarapu, H. Beratan, S. Trolier-McKinstry, Ultrafast crystallization kinetics in (Pb,La)($Zr_{0.30}Ti_{0.70}$)O_3 thin films by pulsed excimer laser annealing, Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on, 57 (2010) 2182-2191.
[51] F.K. Lotgering, Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures—I, Journal of Inorganic and Nuclear Chemistry, 9 (1959) 113-123.
[52] R.I. Eglitis, G. Borstel, E. Heifets, S. Piskunov, E. Kotomin, Ab initio calculations of the $BaTiO_3$ (100) and (110) surfaces, J Electroceram, 16 (2006) 289-292.

[53] R.I. Eglitis, Ab initio calculations of $BaTiO_3$ (111) surfaces, Phase Transitions, 86 (2013) 1115-1120.
[54] M.V. Radhika Rao, A.M. Umarji, Thermal expansion studies on ferroelectric materials, Bull Mater Sci, 20 (1997) 1023-1028.
[55] L. Qiao, X.F. Bi, Strain state, microstructure and electrical transport properties of $LaNiO_3$ films grown on Si substrates, Journal of Physics D: Applied Physics, 41 (2008) 195407.
[56] P. Ambrée, F. Kreller, R. Wolf, K. Wandel, Determination of the mechanical stress in plasma enhanced chemical vapor deposited SiO_2 and SiN layers, Journal of Vacuum Science & Technology B, 11 (1993) 614-617.

FIGURE CAPTIONS

Figure 1. Analysis of 40 nm thick BST films on LNO/SiO_2/Si substrates irradiated with 12000 pulses at different laser fluences with a substrate temperature of 500ºC. (a) Numerical simulations illustrating the temporal evolution of temperature at the BST film after irradiation at 50, 65 and 75 mJ cm^{-2}. The laser pulse dependence with time is also given for comparison purposes. The black-dotted line corresponds to the minimum temperature used to define the effective heating time. (b) XRD measurements of BST films treated at 50, 65 and 75 mJ cm^{-2}. AFM images for samples irradiated at (c) 50, (d) 65, and (e) 75 mJ cm^{-2}.

Figure 2. Percentage of {100} texture present in BST films (thicknesses of 40 and 160 nm) laser crystallized on LNO/SiO_2/Si. Fluences of 65 and 75 mJ cm^{-2} were used during irradiation while the substrate was held at a temperature of 500 ºC, and the pulses applied were set to 1200, 12000 and 72000.

Figure 3. 40nm thick BST films on LNO/SiO_2/Si irradiated at 65 mJ cm^{-2} at a substrate temperature of 500ºC. AFM characterization after (a) 1200 and (b) 72000 pulses. (c) θ-2θ scans of the BST films presented in (a) and (b). (d) 2D-XRD analysis of a BST film laser treated at 65 mJ cm^{-2}, a substrate temperature of 500ºC and 72000 pulses.

Figure 4. BST films on LNO/SiO_2/Si with different thicknesses irradiated at 65 mJ cm^{-2} for 72000 pulses at a substrate temperature of 500ºC. SEM images of BST films with thicknesses of (a) 40 nm and (b) 160 nm. (c) XRD measurements of the BST films described in (a) and (b).

Figure 5. (S)TEM characterization of BST films with different thicknesses on LNO/SiO_2/Si substrates after laser irradiation at 65 mJ cm^{-2}, 12000 pulses and a substrate temperature of 500ºC. BST film with a thickness of 40 nm: (a) low magnification cross-sectional ADF STEM image, and (b) HRTEM image of the orange framed region in (a) and its FFT. BST film with a thickness of 160 nm: (c) low magnification cross-sectional TEM image, (d) HRTEM detail corresponding to polycrystalline grains (blue indicated in (c)) and (e) the associated power spectrum, and (f) HRTEM image of an area close to the interface with LNO (indicated by the green rectangle in (c)) depicting amorphous BST.

Figure 6. Temperature simulations of amorphous BST films on LNO/SiO_2/Si substrates for a fluence of 65 mJ cm^{-2}, and a substrate temperature of 500ºC. (a) Temperature evolution with time for BST films with thicknesses of 40 and 160 nm. The solid and dashed lines are representative of the surface and interface temperature profiles, respectively. (b) Temperature distribution with depth inside the heterostructure for BST films with thicknesses of 40 and 160 nm at 30 ns.