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

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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 °C, 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 nm thick films, crystallization was observed after 12,000 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. Films; A. Sol–gel processes; D. $BaTiO_3$ and titanates; Laser crystallization

1. Introduction

Perovskite oxide films are being explored for numerous functional electronic devices [1–4]. As one example, there is ongoing 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

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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.

2. 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 °C for 10 min on a hot-plate and crystallized at 700 °C for 1 min, with a heating ramp of 20 $°C\,s^{-1}$ 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 (Figs. 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 °C 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 °C 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