Characteristics of the surface layer of barium strontium titanate thin films deposited by laser ablation

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Ba0.5Sr0.5TiO3 (BST) thin films grown on Si by an in situ ultraviolet-assisted pulsed laser deposition (UVPLD) technique exhibited significantly higher dielectric constant and refractive index values and lower leakage current densities than films grown by conventional PLD under similar conditions. X-ray photoelectron spectroscopy (XPS) investigations have shown that the surface layer of the grown films contained, besides the usual BST perovskite phase, an additional phase with Ba atoms in a different chemical state. PLD grown films always exhibited larger amounts of this phase, which was homogeneously mixed with the BST phase up to several nm depth, while UVPLD grown films exhibited a much thinner (~1 nm) and continuous layer. The relative fraction of this phase was not correlated with the amount of C atoms present on the surface. Fourier transform infrared spectroscopy did not find any BaCO3 contamination layer, which was believed to be related to this new phase. X-ray diffraction measurement showed that although PLD grown films contained less oxygen atoms, the lattice parameter was closer to the bulk value than that of UVPLD grown films. After 4 keV Ar ion sputtering for 6 min, XPS analysis revealed a small suboxide Ba peak for the PLD grown films. This finding indicates that the average Ba–O bonds are weaker in these films, likely due to the presence of oxygen vacancies. It is suggested here that this new Ba phase corresponds to a relaxed BST surface layer. © 2000 American Institute of Physics.

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the Ba 3d region acquired at a 45° takeoff angle of as-grown samples at different deposition temperatures are shown in Fig. 2. Each of the Ba 3d3/2 and Ba 3d5/2 peaks can be fitted by two peaks separated by around 1.5±0.1 eV. The lower binding-energy peaks, i.e., 794.2 and 779.0 eV and denoted Ba1, were assigned to Ba atoms in the BST perovskite phase.18–23 The peaks at 795.7 and 780.5 eV and denoted Ba2, were initially thought to be caused by Ba atoms in a decomposed barium carbonate layer.18–21 Since the formation of a carbonate layer on the surface of UV-annealed hydroxyapatite films grown by PLD has been recently reported17 this seemed quite likely to occur here as well. However, while FTIR analysis of hydroxyapatite films17 clearly showed the presence of absorption bands around 1450 cm−1, due to CO32− groups, no such bands were observed here, not even for samples grown at 450 °C, as one can see in Fig. 3. It is worth mentioning that FTIR has been recognized as one of the most sensitive techniques for surface carbonate layer identification22 and that, according to XPS analysis, the surface of this sample, as one can see in Fig. 2, mostly consisted of this new phase (~57%).

While the relative fraction of the Ba2 peak decreased with the increase of the deposition temperature and the use of UV radiation, no such correlation was found for the C 1s peak. Due to charging during XPS investigations, the position of the peaks was shifted from their reference values. The C 1s binding energy cannot be used as a reference in our particular case as we do not know whether this signal was caused by adventitious hydrocarbon usually present on the surface even in ultrahigh vacuum conditions, or was caused by the formation of a chemical compound. Upon assigning the Ba1 peak a binding energy corresponding to stoichiometric BST, i.e., 779.0 eV, one obtains 529.6 and 285.0 eV for the O 1s peak and C 1s peaks, respectively. The binding energy for O 1s is well within the accepted range for BST compounds,18–24 while that of C 1s is much closer to that of adsorbed hydrocarbon (284.6 eV in our XPS system), than that of ~288.6–289.5 eV usually measured for carbon in BaCO3.18–21

Taken at a takeoff angle of 20° in order to enhance surface contribution, the spectra for the Ba 3d region for samples grown at 550 °C are displayed in Fig. 4. One can see that while for the PLD grown samples the ratio of Ba1 to Ba2 peak intensities remained almost constant, at around ~41%, it increased significantly for the UVPLD grown sample, from ~30% to ~44%. This suggests that the surface layer of PLD grown film consists of a rather homogeneous
mixture of these two phases which extends more than 4.0 nm inside the sample depth, while it is only a very thin film (~1 nm) uniformly covering the BST phase for the UVPLD grown sample.

After 6 min sputtering with 4.0 keV Ar ions, which removed accordingly to VASE measurements around 6.0 nm of material, only a very low C contamination was found on the surface, probably caused by the vacuum system itself. The XPS analysis showed that the Ti signal now evidenced the presence of a small contribution from a Ti$^{3+}$ state caused by loss of oxygen due to ion bombardment.\textsuperscript{18,24} The Ba 3d peak of the UVPLD grown sample showed only the presence of the BST phase (Ba1) as one can see in Fig. 5, confirming previous results that Ar ion bombardment at such low energies is not inducing changes in Ba oxidation state for stoichiometric BST films.\textsuperscript{18,24} However, the Ba 3d peak collected from the PLD sample showed the presence of a lower oxidation state, as one can see in Fig. 5, which suggests that for these films a fraction of the Ba–O bonds are somehow weaker, because of oxygen vacancies and residual defects. It is interesting to note that XRD investigations have shown that the lattice parameter of PLD grown films was around 3.96 nm, very close to the 3.95 nm value recorded from BST powder used to make the targets. The UVPLD grown film exhibited a significant higher value, of around 3.98 nm, which shows that these films are strained. XPS analysis indicated that PLD grown films have less oxygen atoms than UVPLD grown films, which should have resulted in films with a larger lattice parameter,\textsuperscript{4,5} quite the opposite of what was observed. A possible explanation could be that the BST film grown by PLD has relaxed near the surface region in a different phase, where Ba atoms are located in a different chemical environment than in perovskite BST.

In summary, we have shown that the surface layer of BST films grown by laser ablation exhibits two chemically different Ba containing phases. The newly formed phase is not a barium carbonate compound which could be etched away by an acid dip but a relaxed BST phase, probably caused by oxygen vacancies and residual defects. The presence of this phase affects the electrical and optical properties of the grown films, especially for very thin films, where its relative contribution is more important. The lower content of this phase in UVPLD grown films can explain their overall better optical and electrical properties. This can also explain previous results that have shown that either annealing treatments under oxygen\textsuperscript{5,9} or even under N$_2$\textsuperscript{25} or a plasma etching of the surface\textsuperscript{26} resulted in dramatic improvements of the electrical properties of BST films.

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