Thin Solid Films 612 (2016) 369–372

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Growth of (100)-highly textured $BaBiO_3$ thin films on silicon

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ARTICLE INFO

Article history:
Received 19 February 2016
Received in revised form 14 June 2016
Accepted 15 June 2016
Available online 16 June 2016

Keywords:
$BaBiO_3$
Textured growth on silicon
Oxide heterostructures

ABSTRACT

We report on the growth and characterization of non-epitaxial but (100)-highly textured $BaBiO_3$ thin films on silicon substrates. We have found the deposition conditions that optimize the texture, and show that the textured growth is favoured by the formation of a BaO layer at the first growth stages. X-ray diffraction Φ-scans, together with the observation that the same textured growth is found on films grown on Pt and SiO_2 buffered Si, demonstrate the absence of epitaxy. Finally, we have shown that our (100)-oriented $BaBiO_3$ films can be used as suitable buffers for the growth of textured heterostructures on silicon, which could facilitate the integration of potential devices with standard electronics.

The progress made during the last decade in the growth of high quality epitaxial oxide heterostructures allowed the discovery of a 2-dimensional electron gas (2DEG) at the interface between the perovskites $SrTiO_3$ and $LaAlO_3$ [1] along with a variety of phenomena such as superconductivity [2] and magnetic order [3], paving the way for the development of oxide electronics novel devices. Some reports claim that this 2DEG is associated to the electronic reconstruction at the interface, related the existence of the so-called "polar catastrophe" [1]; however, other studies point to a less sophisticated scenario associated to the presence of oxygen vacancies [4,5]. Recently, it has been theoretically proposed that a different 2DEG mechanism may be present at the (001) Bi-terminated surface of the perovskite $BaBiO_3$ (BBO) [6], a well-known superconducting perovskite when doped with potassium or lead [7,8]. This effect may arise from the breaking of the charge ordered (insulating) BBO ground state due to the incomplete oxygen environment of the surface cations. The experimental confirmation of this effect remains extremely challenging, mainly due to the difficulty of growing high quality Bi-terminated BBO epitaxial thin films with very low strain, as it can be expected that a moderate amount of strain (as that achievable if, for example, ordinary MgO or $SrTiO_3$ crystals are used as substrates [9,10]) should significantly modify the electronic properties of the material and destabilize these surface effects.

In this paper we follow a different approach by growing and characterizing non-epitaxial BBO thin films on silicon substrates. We show that, under optimal growth conditions, the films are strain free and highly textured in the (100) direction. We demonstrate the absence of epitaxy by means of X-ray diffraction. X-ray photoemission spectroscopy shows the presence of an anomalous Bi-related signal, which we assign to surface Bi-ions with different properties from their bulk counterparts. We also suggest that the (100)-texture of the films is associated to the segregation of a BaO layer at the BBO-silicon interface along with a low surface energy for this particular orientation. Finally, we show that BBO can be used as a buffer for the growth of (100)-oriented heterostructures. We recall that growing low cost, highly oriented functional oxides on silicon could facilitate the integration of potential novel devices with standard electronics.

BBO thin films were prepared by Pulsed Laser Deposition on (100) Si substrates. BBO powders were prepared by solid state reactions, and a 15 mm diameter target was prepared by pressing the powders at 5 Tons/cm^2 followed by a sintering process at 800 °C for 6 h. A Nd:YAG solid state laser, operating at $\lambda = 266$ nm with a repetition frequency of 10 Hz, was used. The used deposition temperatures and oxygen pressures ranged between 500 °C and 680 °C and 5×10^{-3} mbar and 1×10^{-2} mbar, respectively. The laser fluence was fixed at 2 J/cm^2. Structural characterization was performed by X-ray diffraction by using an Empyrean diffractometer with an ultrafast Pixcel 3D detector from Panalytical. Both the surface and the cross-section of the films were visualized with a Scanning Electron Microscope/Focused Ion

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http://dx.doi.org/10.1016/j.tsf.2016.06.033
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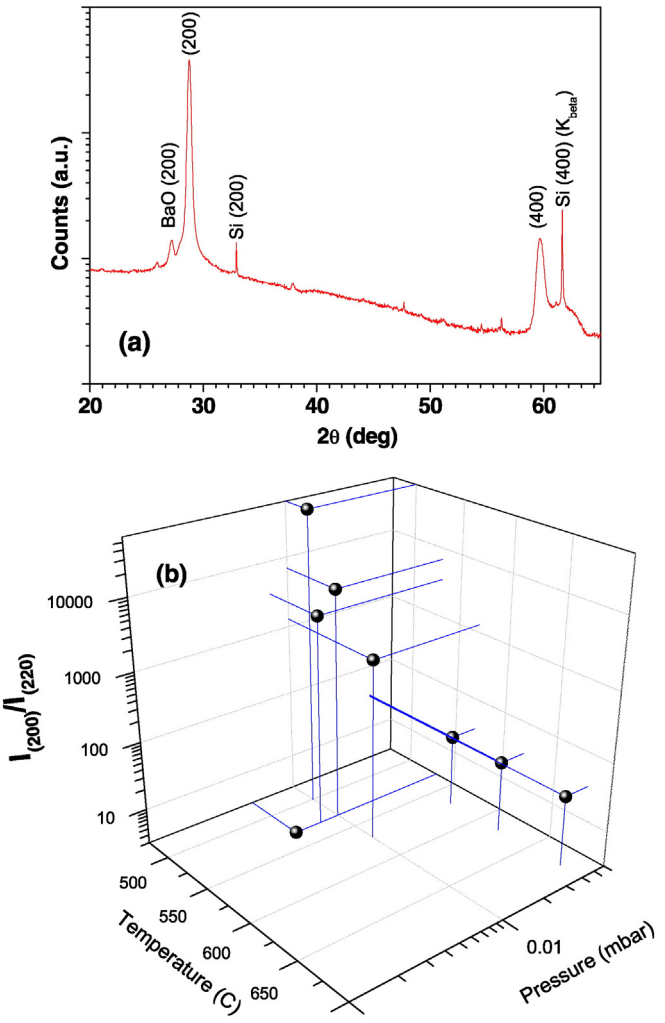

Fig. 1. (a) X-ray diffraction pattern for a 243 nm BBO film grown at 500 °C and an oxygen pressure of 0.01 mbar. A high out-of-plane texture in the (100) direction is evident; (b) Intensity ratio between (200) and (220) XRD reflections as function of both temperature and growth oxygen pressure.

Beam (SEM/FIB) dual beam system (FEI Helios Nanolab 650), operated at a 2 kV voltage. A small volume of material was physically removed with the ion beam, and the remaining cross-section was visualized

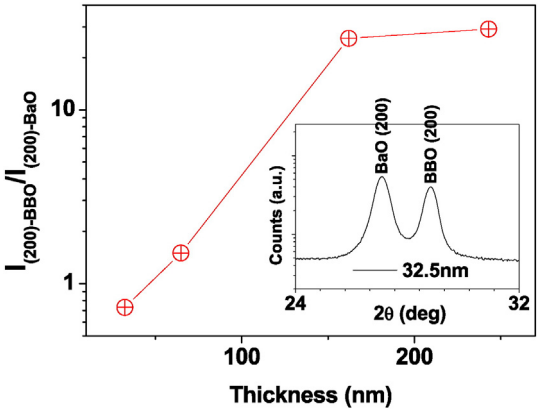

Fig. 2. Intensity ratio between (200) BBO and (200) BaO XRD reflections as a function of the BBO thickness. The inset displays a blow up of a 32.5 nm thick film diffraction pattern, showing that the relative intensity of BaO peak increases as the thickness is reduced. This indicates that BaO segregation takes place close to the interface with the substrate.

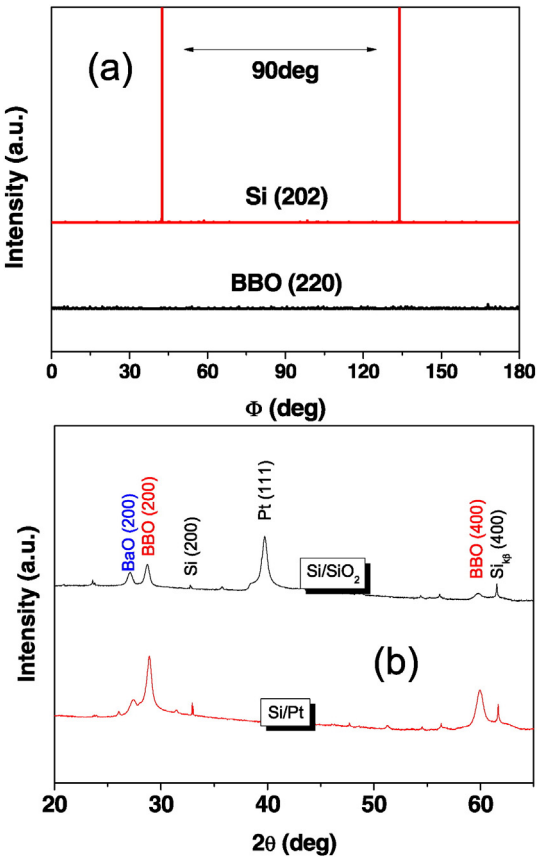

Fig. 3. (a) XRD Φ-scans around Si (202) and BBO (220) reflections, evidencing the absence of in-plane texture; (b) XRD ω-2θ scans for BBO films grown on SiO_2 and Pt buffered Si. A (100) out-of-plane texture is found. Data were shifted for sake of clarity.

with the SEM column, with the sample tilted 52°. For surface visualization, we have also used Carl Zeiss NTS SUPRA 40 microscope. The films morphology was also checked by atomic force microscopy (AFM) by using a NT-MDT microscope. X-ray photoemission spectroscopy (XPS) measurements were performed under UHV conditions (base pressure $< 5 \times 10^{-10}$ mbar) using a SPECS UHV spectro-photometer system equipped with a 150 mm mean radius hemispherical electron energy analyser and a nine channeltron detector. Spectra were acquired at a constant pass energy of 20 eV using an un-monochromated MgKα (1253.6 eV) source operated at 12.5 kV and 20 mA and a detection angle of 30° with respect to the sample normal. Spectral backgrounds were modelled by using Shirley functions, while XPS peaks were fitted with a mixture of Gaussian and Lorentzian (70%/30%) functions.

It is mainly accepted that BBO crystallizes in a monoclinic *C2/m* structure [11], with cell parameters a = 6.1814 Å, b = 6.1360 Å, c = 8.6697 Å and β = 90.1730° (reference pattern 00-035-1020); however, some reports based on electron, X-ray and neutrons diffraction claim that the BBO structure is triclinic with space group *P1* [12,13].

Structural distortions are related to the tilting of the BiO_6 octahedra; in addition, there are also "breathing" distortions where BiO_6 octahedra alternatively expand and shrink along the perovskite structure [11]. These features, along with the charge disproportionation of Bi ions [11] ($2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$) is responsible for the semiconducting behavior of the bulk material. On the other hand, based on Raman spectroscopy experiments performed on a Pb-doped BBO series, Sugai proposed that the insulating character of these materials relies on an alternative mechanism, related to the dimerization of $Bi(Pb)O_{6/2}$ molecules which act as electron traps [14]. Finally, Inumaru et al. reported that the insulating character of the material is maintained even in thin films where the BiO_6 octahedra tilting is suppressed [10].

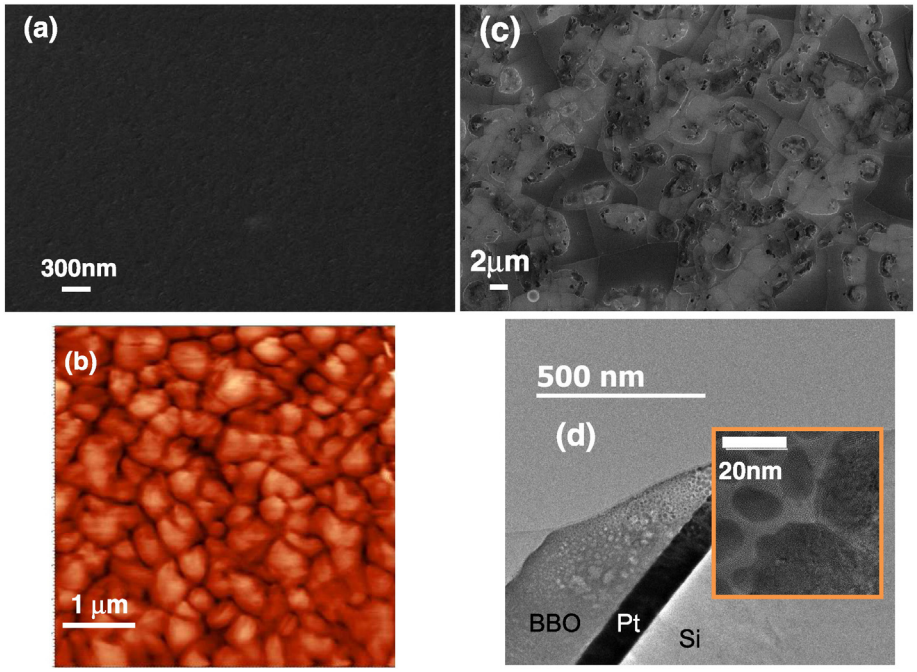

Fig. 4. (a) Scanning electron microscopy images for a 128 nm BBO film; (b) Atomic force microscopy corresponding to a 480 nm BBO film, showing the presence of sub-micrometric grains; (c) Scanning electron microscopy image corresponding to an aged BBO film. The existence of phase segregation at the surface is evident; (d) Transmission electronic microscopy images corresponding to an aged BBO film grown on platinized silicon. The appearance of "bubbles", indicating phase segregation, is seen.

XRD analysis of the obtained films shows that the BBO phase starts to form at deposition temperatures below 620 °C, and parasitic phases are minimized below 570 °C. Fig. 1(a) shows the XRD pattern of a 243 nm BBO film grown at 500 °C and an oxygen pressure of 0.01 mbar. It is found that the film is highly textured in the (100) direction. Furthermore, we found that the texture is highly dependent on the growth conditions, as seen in Fig. 1(b), showing the evolution of the texture, defined as the ratio between the intensities of (200) and (220) XRD reflections, as a function of both the deposition temperature and oxygen pressure. From this figure it can be concluded that the (100) texture is maximized for low temperatures *and* oxygen pressures, being 500 °C and 0.01 mbar the optimum conditions from the set of explored parameters. From the XRD patterns we have extracted an out-of-plane cell parameter $a = (6.18 \pm 0.01)$Å, which is independent of the film thickness and in good agreement with the bulk crystalline structure ($a = 6.1814$ Å), indicating that our films are not strained.

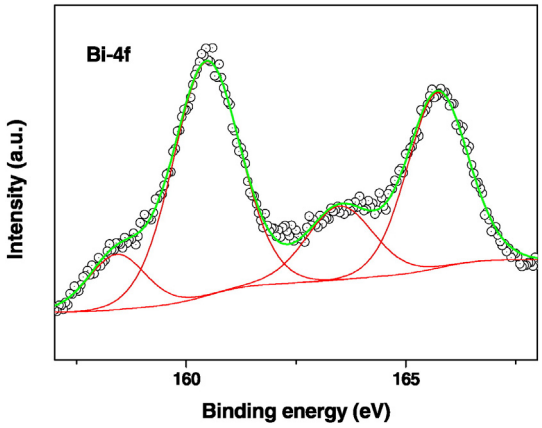

Fig. 5. Bi-4f X-ray photoemission spectroscopy spectrum corresponding to a highly (100)-textured BBO film. Spectral background was modelled by using a Shirley function, while XPS peaks were fitted with a mixture of Gaussian and Lorentzian (70%/30%) functions.

Going back to Fig. 1(a) it should be noted the existence of small XRD reflection around 27°, which we identify as the (200) reflection of BaO (tetragonal *P*4/*nnm* structure, reference pattern 01-078-5719). We

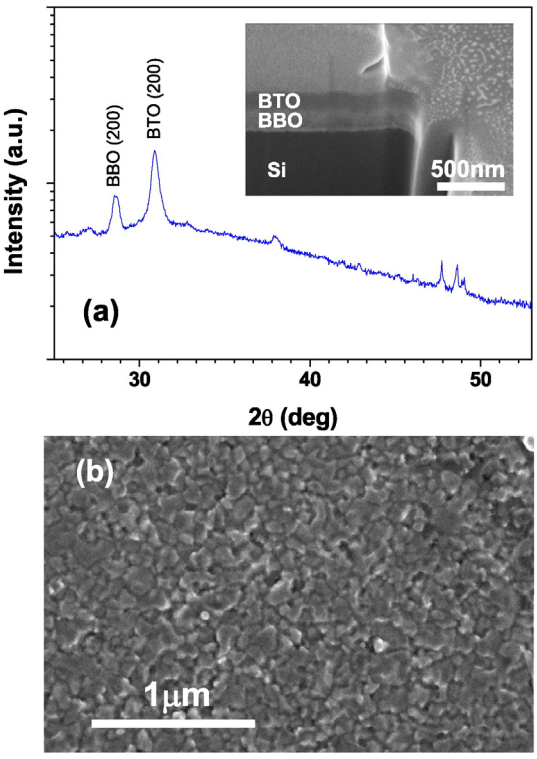

Fig. 6. (a) X-ray diffraction pattern corresponding to a BBO/$BaTiO_3$ bilayer on silicon. BBO imposes its (100)-texture to the $BaTiO_3$ layer. The inset displays a scanning electron microscopy cross-section of the bilayer; (b) Scanning electron microscopy of the surface of $BaTiO_3$ layer, showing a dense arrange of nanosized grains.

notice that if we reduce the thickness of the film, the relative intensity of this impurity peak in relation to the (200) BBO reflections increases, as seen on Fig. 2. This indicates that the BaO segregation is not homogenously distributed in the film but is localized at the substrate-film interface. We recall that Makita et al. reported that if a BaO buffer layer is intentionally grown before the deposition of BBO on $SrTiO_3$ (100) substrates, a strong (100) BBO texture is found [15]. On the contrary, this texture is lost if no buffer is deposited. Our results indicate that this BaO buffer layer is naturally formed at the Si-BBO interface and, consistently with Ref. [15], this contributes to stabilize the (100) texture we have found.

Bearing in mind the strong (100) texture found, it is worth asking about the possible presence of epitaxy between the Si substrate and the BBO films. Although rare, the growth of epitaxial oxides on silicon has been reported for some materials such as YSZ [16–18] and STO [19–20]. In addition, a possible matching between the structures of Si and BBO can be guessed if the (101) BBO diagonal accommodates parallel to the (100) Si cubic structure, spanning two Si unit cells. In order to check that, we have performed XRD Φ-scans around Si (202) and BBO (220) reflections, as shown in Fig. 3(a). The Si (202) scan shows the presence of peaks every 90°, as expected for the cubic Si symmetry. However, the BBO (220) scan shows a constant intensity as Φ is swept, indicating the absence of in-plane texture. The absence of epitaxy is confirmed by Fig. 3(b), which shows X-ray diffraction ω-2θ patterns corresponding to BBO films grown on Si with a 1 μm buffer of amorphous thermal oxide and 100 nm of platinum. In both cases, where epitaxial growth is no possible due to the lack of lattice matching, we have found the same strong (100)-orientation, indicating that this texture is likely related to a low surface energy and that it is not imposed by the substrate by epitaxial growth. This is also consistent with the absence of structural stress mentioned before.

Fig. 4(a) shows a SEM image corresponding to BBO film with a thickness of 128 nm. An homogeneous surface is found with the presence of no particulate. For thicker films, a mosaic-like structure develops, which could reveal the presence of crystallographic domains. The AFM image of Fig. 4(b), corresponding to a 480 nm film, shows the presence of well-connected sub-micrometric grains. The root mean square roughness of the surface was around 5 nm for this thickness. We should also say that the films were found to be chemically unstable. A few weeks after being growth, the surface of the films started to change, as seen in the SEM image of Fig. 4(c), corresponding to an "aged" film, where the appearance of phase segregation is evident (compare with the clean surface of a fresh film, Fig. 4(a)). The aging is also clearly seen by transmission electron microscopy (Fig. 4(d)), where the appearance of segregated phases ("bubbles") distributed in the volume of the film is observed.

Fig. 5 shows the Bi-4f XPS spectrum corresponding to a highly textured film. It is found the presence of two doublets: a dominant doublet at 160.2 eV and 165.8 eV, and a secondary one at 158.1 eV and 163.3 eV. We recall that XPS experiments in bulk samples [21,22] reveal the presence of a single but broad 4f doublet, which cannot be resolved into the two components expected from the Bi charge disproportionation mechanism ($Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$) accepted to occur in bulk BBO. In our case, we attribute the dominant doublet to a bulk-like contribution, and the second one to the presence at the surface of Bi ions with different chemical environment. The origin of this anomalous doublet could be related to a surface electronic effect for the (100) orientation and will be discussed elsewhere.

Finally, we tested the possibility of using the (100)-textured BBO films as a buffer for the growth of oriented heterostructures. For that, we have grown a bilayer of BBO and $BaTiO_3$ on (100) Si. Both layers were grown at the same temperature and oxygen pressure: 500 °C and 0.01 mbar. The XRD pattern of Fig. 5(a) shows that the (100) orientation is maintained in the case of the $BaTiO_3$ layer, showing that BBO is a suitable buffer for the growth of textured heterostructures. The SEM-FIB image of the inset of Fig. 6(a) shows a cross-section of the BBO/$BaTiO_3$ bilayer, with thicknesses of 205 nm and 175 nm, respectively. Fig. 6(b) shows a SEM plane view of the surface of the $BaTiO_3$ layer displaying a dense arrange of nanosized grains.

In summary, we have shown that highly (100)-oriented BBO thin films can be grown on silicon under the right deposition conditions. We show that this texture is not imposed by epitaxial growth and it is probably related to the formation of an interfacial BaO layer at the first growth stages together with a low surface energy for this orientation. XPS measurements suggest the presence of electronic effects at the surface of our (100)-oriented films. Finally, we have shown that these films can be used a suitable buffers for the growth of non-epitaxial but highly oriented heterostructures on silicon, which could facilitate the integration of potentially novel oxide-based devices with standard electronics.

We acknowledge financial support from CONICET (PIP 291) and CIC-Buenos Aires. We thank Dr. D. Vega, from the Laboratory of X-ray Diffraction (GIA, GAIyANN, CAC, CNEA), for the XRD measurements. We also thank Dr. U. Lüders, Dr. O Lebedev and M. Moreau Linares for the 4-circle XRD, TEM and AFM experiments, respectively.

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