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Journal Article

N.B.: When citing this work, cite the original article.

Original Publication:

Petru Lunca Popa, Steffen Sønderby, Sit Kerdsongpanya, Jun Lu, Hans Arwin and Per Eklund, Structural, morphological, and optical properties of Bi₂O₃ thin films grown by reactive sputtering, Thin Solid Films, 2017. 624, pp.41-48.

<http://dx.doi.org/10.1016/j.tsf.2017.01.013>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-136305>

Accepted Manuscript

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PII: S0040-6090(17)30013-5
DOI: doi: [10.1016/j.tsf.2017.01.013](https://doi.org/10.1016/j.tsf.2017.01.013)
Reference: TSF 35725

To appear in: *Thin Solid Films*

Received date: 22 July 2016
Revised date: 22 December 2016
Accepted date: 9 January 2017

Please cite this article as: P. Lunca Popa, S. Sønderby, S. Kerdsonpanya, J. Lu, H. Arwin, P. Eklund, Structural, morphological, and optical properties of Bi₂O₃ thin films grown by reactive sputtering. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Tsf(2017), doi: [10.1016/j.tsf.2017.01.013](https://doi.org/10.1016/j.tsf.2017.01.013)

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**Structural, morphological, and optical properties of Bi₂O₃ thin films grown by
reactive sputtering**

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Abstract

Bi₂O₃ thin films were grown using reactive RF sputtering from a metallic Bi target. The influence of various deposition parameters (substrate temperature, applied power on target and oxygen content in the working gas) on the morphology, structure and optical properties of films was investigated. Depending on the O₂/(Ar+ O₂) ratio of the working gas, bismuth, δ - Bi₂O₃, α - Bi₂O₃ or a mixture of these phases can be deposited, with a narrow window for growth of [111]-oriented δ -Bi₂O₃ thin films. The δ -Bi₂O₃ phase is stable from room temperature up to 350 °C (in air), where an irreversible transition to α -Bi₂O₃ occurs. This phase transformation is also shown to occur during TEM sample preparation, because of the inherent heating from the ion-milling process, unless liquid-nitrogen cooling is used.

Keywords

Bismuth oxide, reactive sputtering, phase transition

1. Introduction

Bismuth oxide is of interest in various technological fields as gas sensors, oxygen pumps, fuel cells and other applications where conduction by oxygen vacancies is required. Bi_2O_3 has six polymorphs: α (monoclinic), β (tetragonal), γ (cubic body-centered), δ (cubic face centered), ε (orthorhombic) [1] and ω (triclinic) [2]. Among these, α and δ are of particular interest. The α -phase (also called bismite) has a high refractive index and one of highest third optical non-linearity which makes it a suitable candidate for optical nonlinear devices such as wavelength converters, optical switches, ultra-short pulse generators and nonlinear optical fiber devices [3,4]. The δ -phase is an exceptional ionic conductor, with two orders of magnitude higher ionic conductivity than that of Yttria Stabilized Zirconia (YSZ), the most used electrolyte in Solid Oxide Fuel Cells (SOFCs). The high ionic conductivity of δ - Bi_2O_3 was attributed to the high polarizability [5] of Bi^{3+} ions and to the high degree of disorder [6,7] in the oxygen sub lattice in a defective fluorite structure. [8-11]. However, in bulk, the δ -phase of Bi_2O_3 is stable only between 825°C (the melting point of bismuth oxide) and 729°C where it transforms into other phases with much lower ionic conductivity. This lack of stability and high temperature range constitutes a major impediment in using δ - Bi_2O_3 as electrolyte in SOFCs. Consequently, much research is focused on lowering the SOFCs operating temperature [12-16].

The stability region of δ - Bi_2O_3 can be extended to lower temperatures by doping the Bi_2O_3 with various elements, especially lanthanides [17, 18] or transition metals [19-22] but this results in a large reduction in ionic conductivity, a consequence of the increasing order within unoccupied oxygen sites. A new method to stabilize the δ -phase with further increase of conductivity consists in the use of highly coherent interfaces of alternating layers of Er_2O_3 -stabilized δ - Bi_2O_3 and Gd_2O_3 -doped CeO_2 . [23]

The most used methods in the synthesis of Bi_2O_3 thin films are chemical vapor deposition [24,25], sputtering [26-30], electrodeposition [31,32], electrophoretic deposition [33] and sol gel methods [34]. There are rather few studies [24, 26,27,35] about the influence of the influence of deposition parameters onto the structure and morphology of Bi_2O_3 deposited films. In our previous work [36], we reported the synthesis of phase-pure and highly oriented $\delta\text{-Bi}_2\text{O}_3$ thin films stable at room temperature for a very narrow range of deposition parameters. In the present paper, we further investigate how the structure, phase composition, morphology, and optical properties of Bi_2O_3 thin films are influenced by substrate temperature, applied power on the target and the oxygen content in the working gas.

2. Experimental procedures

The films were grown by reactive RF magnetron sputtering onto Si (100) and Al_2O_3 (0001). Prior to deposition, the substrates were ultrasonically cleaned in acetone and isopropanol for 10 minutes and then blown-dried using nitrogen. They were inserted into the chamber mounted on a molybdenum holder with adjustable rotation speed and heated through a pyrolytic boron nitride heater. A calibration curve for substrate temperature was obtained prior to deposition by attaching an external thermocouple to an empty substrate. Heating rate was $100^\circ/3\text{min}$. The holder is positioned above the target with a cathode-to-substrate separation distance around 15 cm. The target (Bismuth, 99.99% purity from Mateck GmbH) was mounted in a water-cooled magnetron mounted at a 45° angle with respect to the rotation axis of the sample. A more detailed description of the deposition chamber can be found elsewhere [37].

The working gas was a mixture of high purity argon and oxygen. The total flux of mixed gases was 40 standard cubic centimeters per minute (sccm) except for some control

experiments mentioned bellow where the flow was 25 sccm. The $O_2 / (O_2+Ar)$ flow ratio was controlled by digital gas flow meters while the total pressure in the deposition chamber during deposition was monitored by a capacitance manometer (Baratron). During the sputtering process the pressure was 0.1 Pa. The base pressure was 3×10^{-6} Pa. The sputtering was carried out with a fixed load power source (Advanced Energy RFX-600). The DC self-bias voltage on the bismuth target was constantly monitored. Before each deposition, presputtering of the target in pure argon atmosphere for 30 min was performed in order to remove the oxidized layer on the Bi target surface, and the substrates were held at the intended deposition temperature for the same time in order to achieve thermal equilibrium between the heater and the substrates. The depositions were carried out for 30 minutes (unless otherwise mentioned) corresponding to a film thickness of 300 nm (measured by scanning or transmission electron microscopy-SEM or TEM)

The structure of deposited films was investigated using Philips diffractometers equipped with a Cu K_α X ray source ($\lambda=1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. Pole figures were acquired in azimuth angle (Φ) range $0 - 360^\circ$ and tilting angle (Ψ) range of $0 - 90^\circ$. In situ annealing measurements were performed at 5×10^{-3} Pa with a heating rate of $50^\circ/\text{min}$.

SEM investigations were performed in Secondary Electron mode with a system LEO 1550 using an acceleration voltage of 5 kV. TEM was performed using an analytical high resolution electron microscopy FEI Tecnai G2 TF20 UT with a field emission gun operated at 200 kV and point resolution of 0.19 nm. The TEM samples were prepared by gluing two pieces of samples face to face together, cutting into slice, then polishing, and finally ion milling to electron transparent. Ion milling was run at 5 keV for an angle of 8° with respect to the surface of the sample and at 2 keV and a lower angle (2°) for the last 10 minutes. For

some samples (mentioned in results and discussion sections) ion milling was performed with liquid nitrogen cooling in order to exclude any heating effect on the structure of the samples.

For optical measurements a dual rotating-compensator spectroscopic ellipsometer was used (RC2, J.A. Woollam Co., Inc.) in the spectral range 0.73-5.06 eV at angles of incidence 45°, 55° and 65°. Modeling was performed with the software CompleteEASE (J.A. Woollam Co., Inc.) in a four-layer model: Si substrate/4 nm SiO₂/Bi₂O₃ layer/roughness layer. Database optical data were used for Si and SiO₂ [38]. The complex-valued dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ of the films were modelled with a Tauc-Lorentz dispersion model [39] providing the bandgap. Similar to the method used in ref [35] we include an additional Lorentz model to account for additional absorption bands and to improve the bandgap determination. It should be pointed out that the obtained optical properties are effective dielectric functions for a mixture of several phases, especially for the sample containing Bi. Best-fit parameters were obtained by minimizing the mean squared error (MSE) between model and experimental data. The software uses the Levenberg-Marquardt fitting algorithm and delivers best-fit parameter values and 90% confidence intervals. The confidence intervals are small indicating small correlations among fit parameters.

3. Results and discussion

Influence of substrate temperature

Fig. 1 shows θ -2 θ x-ray diffractograms (Fig. 1a-e) and corresponding SEM micrographs (Fig. 1f-j) for samples grown on Si substrates at room temperature, 175 °C, 300 °C, 400 °C, and 500 °C. All other parameters were kept the same: 30 W applied power on the Bi target, 40 sccm working gas, O₂/ (O₂+Ar) ratio 20%. The DC self-bias was -120 V for all depositions. Fig. 1a, corresponding to the sample deposited at room temperature, shows only a

broad feature centered on $2\theta=27^\circ$, indicating an X-ray amorphous film, as expected at room temperature. The sharp peak at $2\theta=33^\circ$ is the Si substrate **200** peak. The corresponding SEM image (Fig. 1f) shows a uniform deposit, with elongated islands with length around 50 nm and width below 10 nm.

The films deposited at 175°C consist of a mixture of bismuth and $\alpha\text{-Bi}_2\text{O}_3$ phases; the following peaks could be identified [40,41] (Fig. 1b) : Bi **003** ($2\theta=22.5^\circ$), **006** ($2\theta=45.9^\circ$), **012** ($2\theta=27.2^\circ$), **024** ($2\theta=56.0^\circ$), **110** ($2\theta=39.7^\circ$); $\alpha\text{-Bi}_2\text{O}_3$ **012** ($2\theta=28.0^\circ$), **024** ($2\theta=57.8^\circ$) **112** ($2\theta=37.9^\circ$), **302** ($2\theta=44.6^\circ$) and **142** ($2\theta=51.3^\circ$). This phase-mixture can be observed also in the corresponding SEM micrograph (Fig. 1g) where small circular islands (bright spots with diameter ≈ 30 nm) are randomly distributed over a predominant phase consisting of irregular larger grains ($\approx 100\text{-}150$ nm).

The morphology of the films changes dramatically when the substrate temperature is increased above 300°C (Fig. 1c). Besides the peaks corresponding to Bi **012**, **024** ($2\theta=27.2^\circ$ and 56.0°) and to $\alpha\text{-Bi}_2\text{O}_3$ **012**, **024** ($2\theta=28.0^\circ$ and 57.8°), a new strong peak appears at $2\theta=25.8^\circ$ which can be attributed to $\alpha\text{-Bi}_2\text{O}_3$ **002**. At this temperature, the bismuth adatom mobility is high and thus probability for oxide formation increases, explaining why α -phase is predominant. For these samples crystalline grains are clearly defined and two different phases are distinguished easily (Fig. 1h). The SEM micrograph shows a mixture of two phases: a minor one (bismuth) formed by small, almost pentagonal shaped islands, having a size around 200 nm surrounded by a second compact phase (α).

For films deposited at a substrate temperature of 400°C , the XRD scan (Fig. 1d) shows mainly same peaks as in previous case but with different intensity ratios. The corresponding micrograph (Fig. 1i) illustrates a similar mixture of two phases but now with comparable grain sizes. By further increasing the temperatures up to 500°C only Bi **012** and a faint α **012** peak are still observable (Fig. 1e). Moreover, a peak appears at $2\theta=29.2^\circ$ which

possibly corresponds to nonstoichiometric bismuth oxide. The corresponding micrograph seems to indicate the presence of only one phase in scanned areas (Fig. 1j). With the increase of substrate temperature from room temperature to 175 °C, the surface mobility of adatoms increases. As shown by the XRD results, besides bismuth, only α -phase is forming in these conditions. The loss of growth of α -phase at a temperature around 500°C cannot be explained by increased strain with temperature as the expansion coefficients are similar (Bi 13.4 and α - $\text{Bi}_2\text{O}_3 \approx 14 \cdot 10^{-6} / ^\circ\text{C}$; for Si $\approx 3 \cdot 10^{-6} / ^\circ\text{C}$ for this temperature range) but rather by the fact that α -phase is thermodynamically stable at lower temperatures [42].

Fig.1 X-ray diffractograms (a-e) and SEM micrographs (f-j) for samples deposited onto Si 100 substrates at different temperatures. Peak intensities in arbitrary units. The horizontal bar is 200 nm, valid for all micrographs

Influence of oxygen content in the working gas

The results of the investigations related to oxygen ratio content in the total working-gas flow are shown in Fig. 2 (XRD patterns in Figs. 2a-f and corresponding SEM images in Figs. 2 g-l). Other deposition parameters are kept at constant values: RF power 20 W, substrate temperature 175°C. All films are deposited on Si 100 substrates (hence the Si 200 peak $2\theta=33.0^\circ$ present in all diffractograms).

At an $O_2/(O_2+Ar)$ ratio of 2.5 % (Fig. 2 a), the oxygen content is too low to form oxides and metallic bismuth is predominant. The diffraction peaks can be attributed to Bi: **012** ($2\theta=27.2^\circ$), **024** ($2\theta=56.0^\circ$), **104** ($2\theta=38.0^\circ$) and **116** ($2\theta=62.2^\circ$) while the peak from $2\theta=27.95^\circ$ can be attributed either to α - Bi_2O_3 **012** or δ - Bi_2O **111** (see section below). The corresponding SEM image (Fig. 2g) shows a uniform deposit with a granular structure, with grain size about 150 – 200 nm. Small bright spots with diameter below 30 nm, uniformly distributed, can be observed. When the oxygen ratio in the working gas flow is increased to 5%, more peaks appear in the diffractogram (Fig. 2b). Besides the previous Bi peaks, new ones are observed at $2\theta=39.8^\circ$ (**110**) and $2\theta=44.5^\circ$ (**015**). More peaks which can be attributed to nonstoichiometric $Bi_2O_{2.75}$ $2\theta=44.5^\circ$ (**114**) and $2\theta=47.1^\circ$ (**200**) [43]. The film is uniform and compact, with irregular grain size (Fig. 2 h). When oxygen ratio further increases to 15 % (Fig. 2c) and then to 17.5% (Fig. 2d), the conditions become more favorable for formation of δ - Bi_2O_3 . The corresponding peak δ - Bi_2O **111** ($2\theta=27.95^\circ$) becomes more intense while those belonging to bismuth phase become weaker. Moreover the δ - Bi_2O **222** ($2\theta=57.7^\circ$) peak appears. The corresponding SEM micrographs (Fig. 2i and j) indicate uniform films with

grains size decreasing with the increase concentration of oxygen. This tendency goes until the complete disappearance of Bi (Fig. 2e) for $O_2 / (O_2 + Ar) = 20\%$ when the films are formed only by a highly textured δ - Bi_2O_3 with a preferential direction growth along **[111]** (see also pole figures, TEM investigations and discussion in the sections below). Both **111** and **222** peaks are clearly defined now and no others peaks are present. By increasing the oxygen flow ratio to 25% (Fig. 2f and 2l) the BiO phase of appears: **003** ($2\theta=27.53^\circ$), **101** ($2\theta=28.2^\circ$), **006** ($2\theta=56.83^\circ$) and **202** ($2\theta=58.4^\circ$). As shown by the SEM micrographs, when increasing oxygen content the films become denser and with smaller grains sizes.

Fig.2 XRD scans (a-f) and SEM micrographs (g-l) for films deposited at different $O_2/(O_2+Ar)$ ratios. Other deposition parameters are kept at same values: RF power 20 W, substrate temperature 175 °C, 40 sccm work gas flow. The horizontal bar is 200 nm, valid for all micrographs

Influence of power applied on target

Fig. 3 Influence of applied power on target. XRD and SEM micrograph for a sample fabricated using: a - 20W; and b - 30 W. The horizontal bar is 200nm

The results for two films deposited at different applied powers (20 W and 30 W) are shown in Fig. 3. The other parameters were kept fixed at the following values: substrate temperature 175 °C, working gas flow 40 sccm and the O₂/ (O₂+Ar) ratio was 20 %. There are substantial differences related to the structure of as deposited films. For 20 W applied power, the films consist of highly textured pure δ -Bi₂O₃ with a preferential direction of growth along **111**. When the power is increased to 30 W the films become a mixture of Bi and α -Bi₂O₃. This is expected assuming that the amount of sputtered Bi atoms scales approximately linearly with the applied target power, rendering the resulting films sub-stoichiometric in oxygen (with respect to the overall film composition). The degree of orientation is decreasing although some preferential directions of growth are still observed for both components (**003** and **012** for Bi; **012** for α -Bi₂O₃). An increase of the film density with increasing power is observed in corresponding SEM micrographs. The mixture of bismuth and α -Bi₂O₃ is observed also in the micrograph in Fig. 3b (corresponding to a power of 30 W): α -phase has a uniform structure while the bismuth is randomly distributed in small islands (brighter spots).

The results of ellipsometry measurements for the films deposited at 20 W and 30 W power are shown in Fig. 4 and Table 1. The film deposited at 30 W was found to be 42% thicker which is expected as deposition rate scales approximately linearly with applied power. The film synthesized at higher power has a lower roughness, possibly because of leveling of the surface due to incident higher-energy species. The δ - Bi_2O_3 films have an optical band gap of around 2.4 eV which is in accordance with Fan *et al.* who reported 2.45 eV [27]. For the $\text{Bi}+\alpha$ - Bi_2O_3 film, the band gap becomes smaller and is around 1.9 eV for this film. This is lower than 2.5 -2.8 eV previously reported for the α -phase [44], most likely due to the fact that the films contain a minority phase of metallic bismuth. The dispersion curves for the refractive index and extinction coefficient are similar of those obtained by Gomez *et al.* [35]. However, our films have slightly higher refractive indices, possibly indicating that they are denser. Similarly to Gomez *et al.*, we have included an interband transition. To reduce the correlation parameter we use only one transition with energy as shown in Table 1. This increases modeling accuracy for bandgap determination but the values of the interband transitions are only indicative and further studies are needed to fully characterize these resonances. We also observe that the fit to the model is better for the δ -phase as the MSE is lower for this sample.

Fig. 4 Dielectric function $\epsilon = \epsilon_1 + i \epsilon_2$ as determined from analysis of ellipsometry data

recorded on Bi₂O₃ films using 20 W (black curve) and 30 W (blue curve) applied power on the target

Table 1. Ellipsometry results for two films grown using two different RF applied powers

Film	δ -Bi ₂ O ₃	Bi+ α -Bi ₂ O ₃
RF power (W)	20	30
Surface roughness (nm)	4.9 $\pm$ 0.1	2.7 $\pm$ 0.1
Layer thickness (nm)	298.0 $\pm$ 0.1	423.2 $\pm$ 0.1
Band gap (eV)	2.360 $\pm$ 0.002	1.862 $\pm$ 0.003
Interband (eV)	3.59	3.21
MSE	3.5	8.2

Deposition of δ -Bi₂O₃ thin films

As described in our previous paper [36] and briefly summarized here for completeness, highly oriented pure δ -Bi₂O₃ films can be deposited both on silicon and sapphire substrates for a very narrow range of deposition parameters (150–200°C, 18%–20% of O₂/ (O₂+Ar) ratio in the sputtering gas and 20 W applied power on target). Fig. 5 a (from Ref. 36) shows XRD patterns for films deposited in same batch onto Si and Al₂O₃. Beside the peaks characteristic to the substrates Si **200** ($2\theta=33.1^\circ$), Si **400** ($2\theta=69.2^\circ$), Al₂O₃ **006** ($2\theta=42.0^\circ$) there two more peaks at 2θ positions 28.0° and 57.4° . Monoclinic alpha [40], tetragonal beta [45] and cubic delta [46] phases of Bi₂O₃ present all very close diffraction peaks around these 2θ positions and thus for a precise phase identification a XRD texture analysis was performed (Fig. 5.b, from Ref. [36]). The diffraction rings observed at $\Psi=70^\circ$

($2\theta=28.0^\circ$), $\Psi=54^\circ$ ($2\theta=32.4^\circ$) and $\Psi=35^\circ$ ($2\theta=46.6^\circ$) prove the cubic crystal geometry of films and hence the presence of $\delta\text{-Bi}_2\text{O}_3$.

Fig.5 (From Ref. 36) $\delta\text{-Bi}_2\text{O}_3$ films. **a** XRD θ - 2θ patterns for films deposited onto Si (100) (red) and Al_2O_3 (0001) (black) substrates; **b** pole figures for 2θ positions of 28° , 32.4° and 44.6° .

Two important observations in the effort to explain the formation of $\delta\text{-Bi}_2\text{O}_3$ in these conditions: this phase is obtained in a very narrow window of deposition parameters values and it exhibits higher thermal stability in air than in vacuum [36]. First, there is competition between the thermodynamics of the process and the surface kinetics, meaning that formation of δ -phase with its simpler cubic stacking (compared to monoclinic α -phase) is kinetically favored at substrate temperature of around 200°C . Second, the δ -phase can accommodate a degree of vacancies on oxygen sites and therefore provides a mechanism for increased stability relative to the α -phase.

After this summary of the results from Ref. 36, we proceed with further TEM characterization. Figure 6 shows TEM images for two Bi_2O_3 films from the same deposition batch, both exhibiting $\delta\text{-Bi}_2\text{O}_3$ films in the as-deposited state. For the first film, liquid

nitrogen cooling was used during the ion milling process (Fig. 6a from Ref. [36]). It has a columnar structure with thickness of 300 nm and ~50 nm column diameter. HRTEM and SAED images indicate a highly textured film with a preferential growth direction along [111]. However, an important result is observed for samples that were prepared with ion milling without any cooling: after TEM sample preparation, the films now present a monoclinic α structure (Fig. 6 b). This shows that the inherent heating from the ion-milling process exceeds the temperature required to transform the samples from δ to α ; for ex-situ annealing, the $\delta - \alpha$ phase transition was observed to take place around 260°C. The volume of the α crystal is noteworthy, as only one crystalline grain can be observed in the TEM images, i.e., the observed α grain covers the entire film thickness and is at least 300 nm wide (the limits of electron transparency of the TEM sample). These results show that the inherent heating of the ion-milling process transfers sufficient energy to the film to transform from the metastable δ -phase into the more thermodynamically stable α -phase. As further supported by our previous annealing experiments [36], this transition is affected by the surrounding environment, as we observed for ex-situ annealing experiments (i.e. in atmospheric conditions) the transition taking place around 350 °C while for in-situ annealing in vacuum, the same transition was observed around 260°C .

These results emphasize the need for care during sample preparation not only of δ - Bi_2O_3 , but also more generally for metastable materials with a stability limit in the same range as the inherent heating caused by the ion-milling process.

Fig.6 TEM investigations on δ - Bi_2O_3 samples **a** (from Ref. 36) TEM, HRTEM and SAED images for a sample prepared using nitrogen cooling during ion milling process. **b**. TEM, HRTEM and SAED for a sample prepared using normal ion milling.

V.CONCLUSIONS

Bi_2O_3 films were synthesized by RF reactive sputtering and the influence of substrate temperature, applied power on target and oxygen content in the working gas on the structure morphology and optical properties of the films was investigated. The main effect of substrate temperature is the changing grain size due to different bismuth adatoms mobility on the surface. Both applied power and oxygen content alter the oxygen/bismuth ratio. By changing any parameter related to this ratio a change in the properties of the films is obtained. There is a narrow process window where highly oriented phase-pure δ - Bi_2O_3 films are obtained. These are stable to 260 °C (in vacuum) or 350 °C (in atmosphere) before transforming to α -phase. This phase transformation can also occur during TEM sample preparation, because the inherent heating from the ion-milling process exceeds the temperature required to transform the samples from δ to α -phase. This emphasizes the need for care in sample preparation also more generally for metastable materials.

Acknowledgments

We acknowledge support from the Swedish Foundation for Strategic Research (Future Research Leaders 5), Nordforsk Ref. No. 9046 (ThinSOFT), Nordic Innovation Centre Ref. No. 09046 (Thin-SOFC), the European Research Council (ERC) under the European Community's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 335383, and the Swedish Research Council (VR) under Project No. 2012-4430.

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Highlights

- Influence of deposition parameters on as grown films' properties was investigated
- By tuning the O/Bi atomic ratio, Bi, δ -Bi₂O₃, α - Bi₂O₃ or mixtures can be deposited
- There is a narrow process window where high oriented pure δ -Bi₂O₃ films are obtained
- Delta-alpha phase transformation can occur during TEM sample preparation