

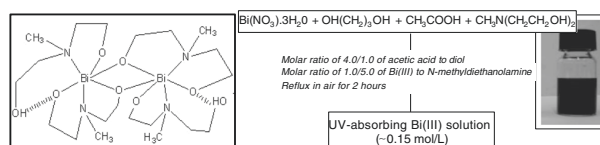
## Photochemical solution deposition of $\beta$ - $\text{Bi}_2\text{O}_3$ thin films

Dulce Perez-Mezcua<sup>1,2</sup> · Iñigo Bretos<sup>1</sup> · Ricardo Jiménez<sup>1</sup> · Jesús Ricote<sup>1</sup> · Rafael José Jiménez-Rioboó<sup>1</sup> · Cosmelina Gonçalves da Silva<sup>3</sup> · Daniel Chateigner<sup>3</sup> · Luis Fuentes-Cobas<sup>4</sup> · Rafael Sirera<sup>2</sup> · M. Lourdes Calzada<sup>1</sup>

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**Abstract** The non-equilibrium  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph is stabilized in thin films by a photochemical synthesis method. A strong ultraviolet-absorbing bismuth(III)-*N*-methyl-diethanolamine complex is synthesized in solution as an ideal precursor for the  $\beta$ - $\text{Bi}_2\text{O}_3$  phase. Ultraviolet-light induces the formation of an amorphous —Bi—O—Bi— continuous network in the films deposited from the former solution that easily converts into the  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph at a temperature as low as 250 °C. The room temperature stabilization of the  $\beta$ - $\text{Bi}_2\text{O}_3$  phase is confirmed by their structural characterization using four-circle X-ray diffractometry. This study unequivocally identified the tetragonal crystal structure of the  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph in the films. The high phase purity of these  $\beta$ - $\text{Bi}_2\text{O}_3$  films is responsible for their exceptional visible-light photocatalytic activity, thus enabling the applications of the films of this metastable phase at room-temperature conditions.

**Graphical Abstract** Photosensitive precursor solutions containing a photosensitive Bi(III)-*N*-methyl-diethanolamine complex lead to the stabilization of the high-temperature  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph in films on Pt-coated silicon substrates prepared at a low temperature of 250 °C using UV-irradiation.



**Keywords** Photochemistry · Sol-gel · Metastable phases ·  $\beta$ - $\text{Bi}_2\text{O}_3$  · Room-temperature stabilization · Thin films · Low-temperature processing · Thin films

### 1 Introduction

Bismuth is one of the less toxic heavy metals. This has increased the interest in the bismuth containing materials with functional properties that can be applied in thermoelectrics, ferroelectrics, or multiferroics. Besides, the binary oxides of bismuth (III) show functionalities that make them potential candidates for their integration in sensors, catalysts, or solid electrolytes [1]. Several polymorphic forms of  $\text{Bi}_2\text{O}_3$  are reported in the literature, including the  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -,  $\epsilon$ -, and  $\omega$ -phases [1]. Among them, those that have attracted the highest interest are the  $\beta$ - and  $\delta$ - polymorphs. The  $\beta$ - $\text{Bi}_2\text{O}_3$  is the most active heterogeneous photocatalyst of these polymorphs and the  $\delta$ - $\text{Bi}_2\text{O}_3$  has the highest oxidation conductivity of all of the binary metal oxides. However, none of them can be used at room temperature: the cubic

✉ M. Lourdes Calzada  
lcalzada@icmm.csic.es

<sup>1</sup> Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas (ICMM-CSIC), C/ Sor Juana Inés de la Cruz, 3, Cantoblanco, Madrid 28049, Spain

<sup>2</sup> Departamento de Química, Facultad de Ciencias, Universidad de Navarra, Pamplona 31008, Spain

<sup>3</sup> CRISMAT—ENSICAEN and IUT-Caen, Université de Caen Normandie, Caen 14050, France

<sup>4</sup> Centro de Investigación en Materiales Avanzados, Chihuahua 31109, Mexico

$\delta$ - $\text{Bi}_2\text{O}_3$  phase is thermodynamically stable at high temperatures (730–824 °C) and the tetragonal  $\beta$ - $\text{Bi}_2\text{O}_3$  is a metastable high-temperature phase (450–667 °C). Therefore, many efforts have been done for the stabilization at room temperature of these phases following different approaches and with various degrees of success [2–5].

On the other side, the need of integration of high-performance oxides in cheap and flexible substrates has driven the development of low temperature processing methods for functional crystalline oxides [6–10]. Among them, those methods based on the ultraviolet (UV) irradiation of light sensitive metal coordination complexes have shown a huge potential in this area [11–14]. These compounds are characterized by reactive metal to ligand charge transfer states, where a shift of the electronic distribution can be induced by UV light, resulting in the dissociation of the complex bonds and the formation of the metal—O—metal skeleton of the oxide material. Then, the energy provided by UV-light can be used for the formation of crystalline oxide phases far from their equilibrium conditions.

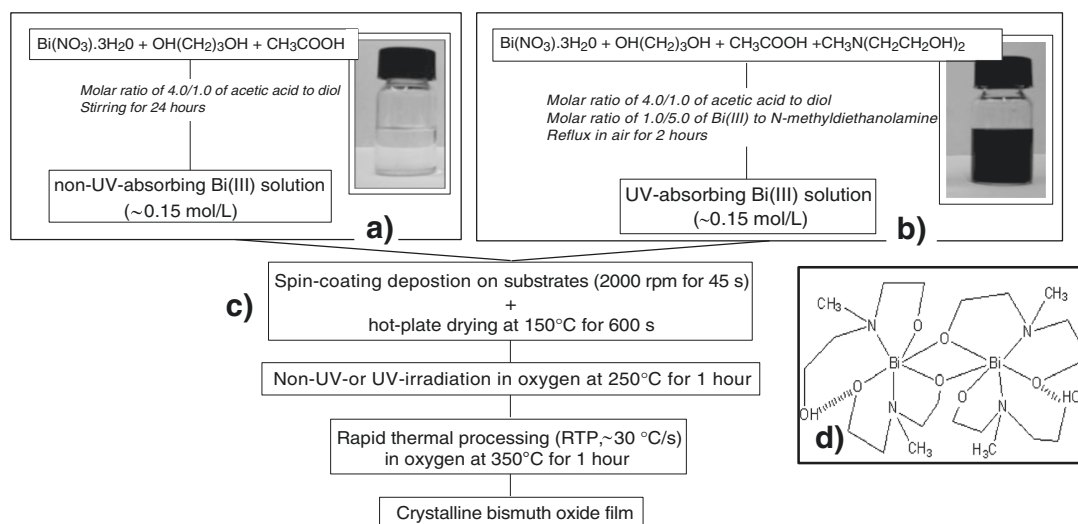
The authors of this work have previously used a sol-gel synthesized photosensitive metal complex between Bi(III) and *N*-methyl-diethanolamine [13, 14] for the low temperature preparation with UV-irradiation of ferroelectric bismuth-based perovskite thin films [14]. Here, we show the room temperature stabilization of the pure  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph in thin films by the low temperature treatment with UV-light of the layers deposited on Pt-coated silicon substrates from solutions containing the former Bi(III)-*N*-methyl-diethanolamine complex. The results obtained turns

this photochemical method into a powerful tool to design and stabilize non-equilibrium crystalline oxide phases at low temperature, successfully demonstrated here for pure  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films. To the knowledge of the authors, pure  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films have not been prepared before at so low temperatures (250 °C). The synthesis of  $\beta$ - $\text{Bi}_2\text{O}_3$  powders have been previously reported [15, 16], but to support these powders on cheap large-area flexible plastics is not straightforward. However, the opportunity of integrating  $\beta$ - $\text{Bi}_2\text{O}_3$  layers directly with cheap and flexible polymers enlarges the applicability of these films to areas until now unexplored for photocatalytic materials (e.g., self-cleaning surfaces, wearable antimicrobial clothes) [17, 18].

The X-ray characterization of these  $\text{Bi}_2\text{O}_3$  thin films deposited on Pt-coated Si substrates using a four circle diffractometer, unequivocally identified the formation of the metastable  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph with a tetragonal crystal structure, not detecting any other crystal phases. Additionally, the films show a good efficiency for visible-light photocatalysis, as expected for pure  $\beta$ - $\text{Bi}_2\text{O}_3$  materials. A deep characterization of the properties and functionality of these films is in progress.

## 2 Experimental section

Non-UV-absorbing Bi(III) and UV-absorbing Bi(III) solutions were prepared following the schemes of Fig. 1 [13, 19]. The non-UV absorbing Bi(III) solution



**Fig. 1** Preparation of  $\text{Bi}_2\text{O}_3$  thin films. **a, b** Schemes for the preparation of the Bi(III) precursor solutions: non-UV-absorbing Bi(III) solution and UV-absorbing Bi(III) solution. **c** Preparation of bismuth oxide thin films. UV-irradiation of the films was carried out with an excimer lamp with  $\lambda_{\text{emission}} = 222 \text{ nm}$  and during heating in oxygen

atmosphere at 250 °C. Crystallization of the films was carried out in a rapid thermal processor (RTP, JetStar 100 JIPELEC equipment) at 350 °C for 1 h in an oxygen atmosphere and with a heating rate of  $\sim 30 \text{ }^\circ\text{C s}^{-1}$ . **d** Molecular structure of the coordination complex formed between Bi(III) and *N*-methyl-diethanolamine ( $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ )

(~0.15 equivalent moles of Bi(III) per liter of solution) was obtained by mixing bismuth (III) nitrate hydrated ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , Aldrich, 99.99%) in 1,3-propanediol ( $\text{HO}(\text{CH}_2)_3\text{OH}$ , Aldrich, 98%) and acetic acid ( $\text{CH}_3\text{COOH}$ , Merck, 100%) and stirring for 24 h in air, using a 1.0/4.0 propanediol/acetic acid molar ratio. A transparent solution was obtained, herein after Bi(III) solution. The UV-absorbing Bi(III) solution (~0.15 equivalent moles of Bi(III) per liter of solution) was prepared by refluxing for 1 h in air bismuth (III) nitrate hydrated with *N*-methyl-diethanolamine ( $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ , Aldrich, 99%) (*mdea*), in 1,3-propanediol and acetic acid solvents (1.0/4.0 diol/acetic acid and 1.0/5.0 Bi(III)/ $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$  molar ratios). A reddish-brown colored sol was obtained, herein after Bi(III)-*mdea* solution.

The  $\text{Bi}_2\text{O}_3$  thin films were obtained on Pt-coated silicon substrates ( $\text{Pt}/\text{TiO}_2/\text{Pt}/\text{SiO}_2/(100)\text{Si}$ ) by the spin-coating deposition of the Bi(III) and Bi(III)-*mdea* precursor solutions. The layers were dried at 150 °C for 10 min and heated at 250 °C in an  $\text{O}_2$  atmosphere, with or without UV-irradiation. For the UV-irradiation, an excimer lamp (Heraeus-Noblelight BlueLight Curing Module) with  $\lambda_{\text{emission}} = 222$  nm, electrical power of 1.5 kW, frequency of 50 Hz, irradiation length of 30 cm and irradiance of  $6.25 \text{ W cm}^{-2}$  was used. Samples were placed in a closed chamber, containing a furnace for heating with a distance of the sample to the UV-lamp of 9 cm. Further thermal treatments of the samples were carried out in a rapid thermal processor (RTP, JetStar 100 JIPELEC equipment).

Micrographs of the crystalline oxide films were obtained by field-emission gun scanning electron microscopy (FEG-SEM, Nova Nanosem 230 FEI Company equipment, Hillsboro, OR). Energy dispersive spectroscopy (EDS) analysis of the  $\text{Bi}_2\text{O}_3$  thin films on  $\text{Pt}/\text{TiO}_2/\text{Pt}/\text{SiO}_2/(100)\text{Si}$  substrates was carried out in this equipment.

The crystallinity of the films was followed by X-ray diffraction (XRD), using a Siemens D500 powder diffractometer with a Cu anode ( $\lambda = 1.5406 \text{ \AA}$ ) and a Bragg-Brentano geometry. Additional X-ray measurements were carried out in a diffractometer equipped with a four-circle opened Eulerian goniometer ( $\chi$ ,  $\varphi$ ), a Cu anode ( $\lambda = 1.5406 \text{ \AA}$ ), a 120° curved linear position-sensitive detector (CPS120 from INEL SA) and a flat graphite primary monochromator. Combined analysis (texture, microstructure using an extended Rietveld refinements) of the XRD data were carried out using the Materials Analysis Using Diffraction package [20].

Film thickness and optical properties were obtained by spectroscopic ellipsometry (SOPRA GES5E ellipsometer) in the wavelength range from 200 to 850 nm. Optical properties ( $n(\lambda)$ ,  $k(\lambda)$  and  $\alpha$ ) were calculated from these data.

The photocatalytic activity of the  $\beta\text{-Bi}_2\text{O}_3$  films was evaluated by the degradation of methylene blue, MB ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot x\text{H}_2\text{O}$ ). A  $\beta\text{-Bi}_2\text{O}_3$  film with  $\sim 2 \text{ cm}^2$  of area

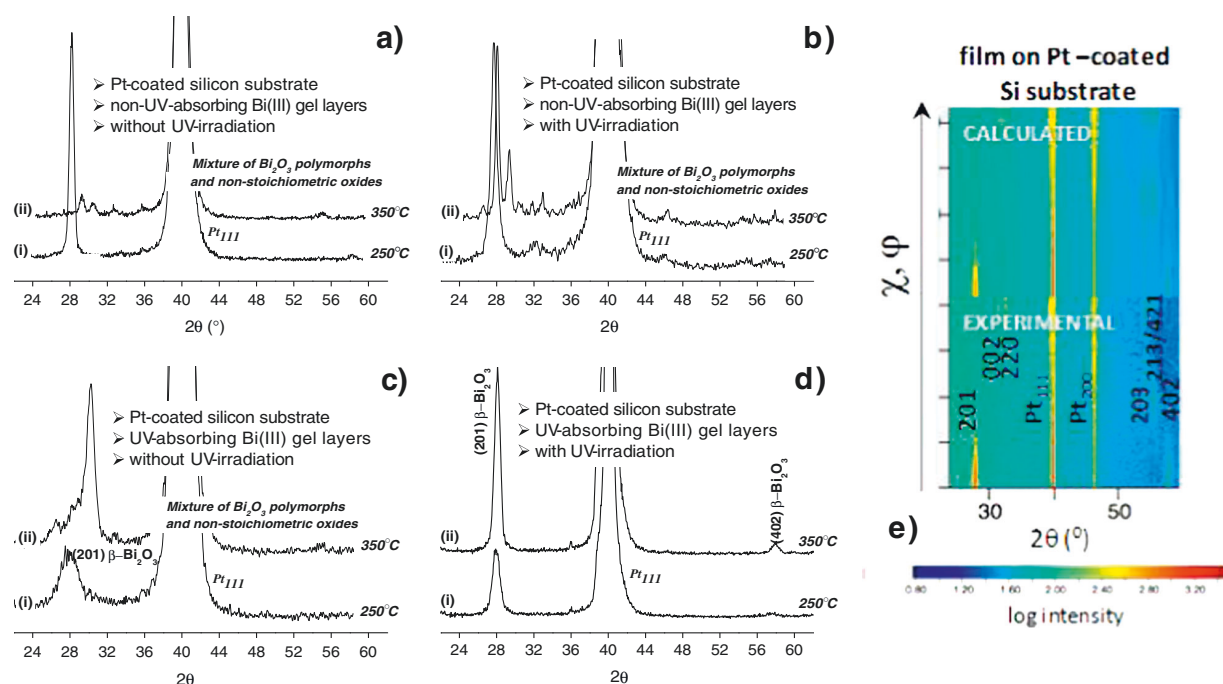
and a thickness of  $\sim 50$  nm was placed inside a chamber with 8 mL of the dye solution ( $10^{-6} \text{ mol L}^{-1}$ ) and with a pH  $\sim 1$ , fixed with hydrochloric acid (HCl). A solar lamp (Ultra-Vitalux 300 W, Osram) emitting in UVA (13.6 W) and UVB (3.0 W) regions was used for the irradiation of the films placed in a closed reactor chamber containing the film immersed in the dye solution. The temperature was kept below 38 °C by a cooling system. Prior to irradiation, the suspension was in the dark for 15 min to reach an adsorption/desorption equilibrium.

### 3 Results and discussion

The Bi(III)-*mdea* photosensitive solutions synthesized as indicated in Fig. 1, gives place to the formation of the metal complex of Bi(III) and *N*-methyl-diethanolamine shown in Fig. 1d [13]. This bismuth(III)-*N*-methyl-diethanolamine complex shows a strong UV absorption at  $\lambda \sim 250$  nm [14], because the alkanolamine ligand is bonded to the Bi(III)  $d^{10}$  cation, forming a compound with reactive metal-to-ligand charge transfer states that are activated under UV irradiation [11, 14]. This promotes the rupture of the organic bonds and the formation of a metal–O–metal chains [21–23]. Hence, the energy provided by the illumination with UV-light of photosensitive precursors turns into a powerful tool for the synthesis of inorganic compounds far from their equilibrium conditions and it has been exploited for the low temperature crystallization of functional (ferroelectric) oxide thin films [7, 11, 14, 21–23].

Therefore, this Bi(III)-*mdea* solution was used for the deposition of amorphous layers on Pt-coated silicon substrates that were UV-irradiated in oxygen at a temperature of 250 °C to attain  $\text{Bi}_2\text{O}_3$  thin films. A crystalline  $\text{Bi}_2\text{O}_3$  phase is obtained in these films at a very low temperature, observing that the crystallinity of the films is improved by the increase of the temperature.

The crystalline structures of the films derived from the Bi(III) and Bi(III)-*mdea* solutions after the UV-assisted low temperature processing were analyzed by XRD, with a conventional  $\theta$ – $2\theta$  geometry (Fig. 2a–d). These patterns show the characteristic (111) peak of the Pt from the substrate and other peaks that correspond to different bismuth oxide phases. In the particular case of the films derived from the photosensitive Bi(III)-*mdea* solutions and irradiated with UV-light (Fig. 2d), two diffraction peaks are recorded at  $2\theta \sim 28^\circ$  and  $2\theta \sim 58^\circ$  that could be assigned to the (111)/(222) or (201)/(402) peaks of the  $\delta\text{-Bi}_2\text{O}_3$  or  $\beta\text{-Bi}_2\text{O}_3$  polymorphs with a preferred orientation along the  $\langle 111 \rangle$  or  $\langle 201 \rangle$  axes, respectively. It must be noted that when UV-irradiation is not used and/or non-UV-absorbing Bi(III) gel layers are deposited, the crystallization at such low temperature leads to an undesirable mixture of  $\text{Bi}_2\text{O}_3$  phases.



**Fig. 2**  $\text{Bi}_2\text{O}_3$  thin films. **a**, **b**, **c**, and **d** X-ray diffraction (XRD) patterns of  $\sim 45$  nm thick  $\text{Bi}_2\text{O}_3$  thin films fabricated on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrates from non-UV-absorbing and from UV-absorbing Bi(III) gel layers. (i) the deposited layers were heated for 1 h at 250 °C in an oxygen atmosphere, without UV-irradiation or with UV-irradiation. (ii) The former layers were subjected to a further rapid thermal annealing in oxygen at 350 °C for 1 h with a heating rate of

30 °C s<sup>-1</sup>. **e** Two-dimensional plot of the measured and calculated pattern for different orientations of the  $\text{Bi}_2\text{O}_3$  thin film which conventional XRD pattern is shown in **d**(ii). This pattern has been obtained at different sample orientations (grid of 5° × 5° in  $\chi$  and  $\varphi$ ) using a four circle goniometer and it confirms that the  $\text{Bi}_2\text{O}_3$  phase formed in this film corresponds to the  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph

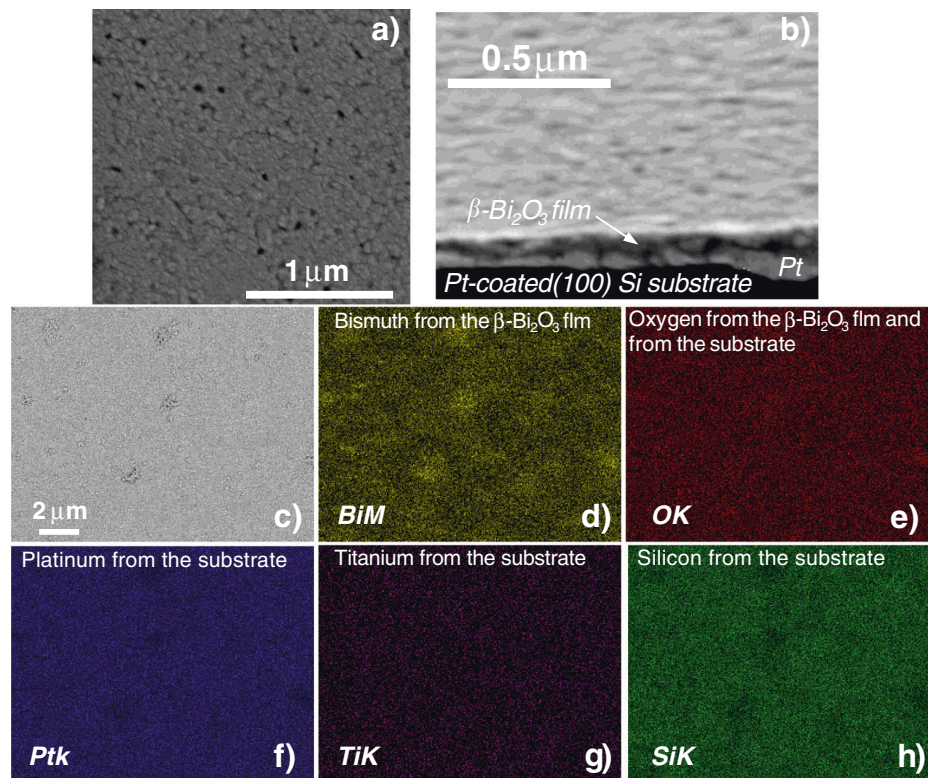
To determine the nature of the polymorph obtained in the films of Fig. 2d, the analysis of the XRD data obtained for a systematic rotation of the sample (grid of 5° × 5° in  $\chi$  and  $\varphi$ ) with a four-circle goniometer was carried out (Fig. 2e). The Combined Analysis refinement [20, 24, 25] carried out on the collected data indicates that the calculated pattern fits to the tetragonal  $\beta$ - $\text{Bi}_2\text{O}_3$  phase, indicating the stabilization of this metastable polymorph in this film. Fig. 2e shows the two-dimensional plot of the measured and calculated patterns for the film on the Pt-coated silicon substrate. A good agreement is obtained using the  $P\bar{4}2_1c$  space group corresponding to tetragonal  $\beta$ - $\text{Bi}_2\text{O}_3$  [Crystallography Open Database n° 9007723] [24, 25], whereas the refinement with  $Fm\bar{3}m$  of the cubic  $\delta$ - $\text{Bi}_2\text{O}_3$  [COD n° 1534843] leads to poor reliability factors [20, 24, 25].

Figure 3 shows the surface and cross-section FEG-SEM images, as well as the EDS analysis, of the former  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films prepared from the Bi(III)-*mdea* solutions with a UV-assisted low-temperature annealing at 350 °C. The films were deposited on Pt-coated silicon substrates (Pt/TiO<sub>2</sub>/Pt/SiO<sub>2</sub>/(100)Si). A homogeneous surface microstructure with an estimated average grain size of 35 nm and a thickness of  $\sim 45$  nm are observed Figs. 3a–b. Fig. 3c corresponds to the low magnification image of the surface of the film where the

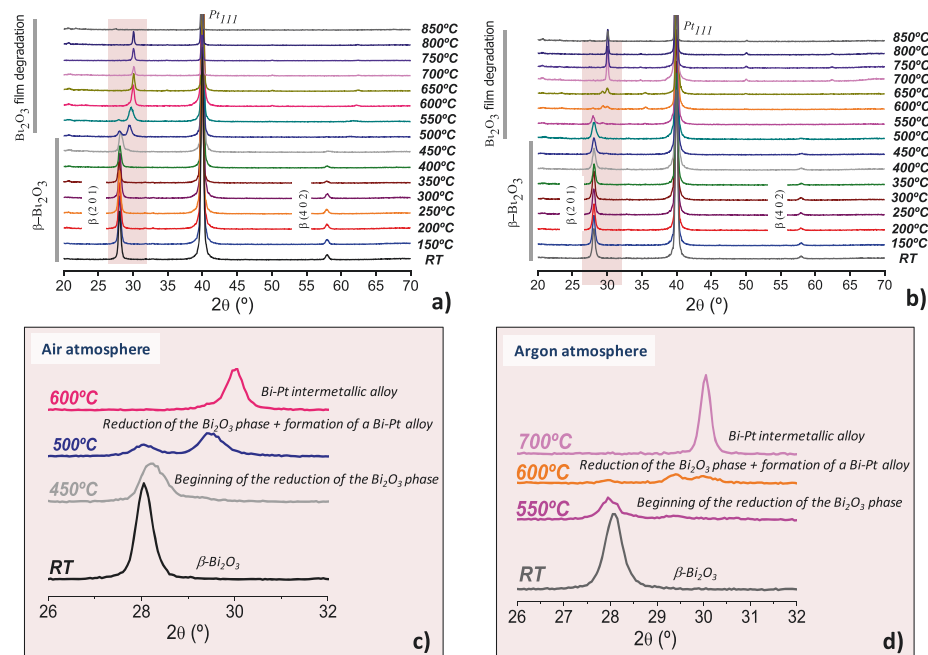
EDS analysis has been carried out. The maps of the distribution of the different elements detected in this surface are shown in Fig. 3d–h. A uniform distribution of bismuth is obtained for the film, indicating that the crystalline  $\beta$ - $\text{Bi}_2\text{O}_3$  films have a homogeneous composition. Homogeneous maps distribution are also obtained for the other elements forming the material analyzed by EDS (the  $\beta$ - $\text{Bi}_2\text{O}_3$  film on the Pt/TiO<sub>2</sub>/Pt/SiO<sub>2</sub>/(100)Si substrate). However, quantitative results about the bismuth to oxygen ratio in the  $\beta$ - $\text{Bi}_2\text{O}_3$  layer cannot be calculated because the oxygen analyzed by EDS corresponds not only to the oxide film but also to the substrate (the TiO<sub>2</sub> buffer/adhesive layer and the native SiO<sub>2</sub> of the silicon wafers).

Figure 4 shows the stability with temperature of these  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films on Pt-coated silicon substrates, in oxygen and argon atmospheres. It should be noted the stability of the polymorph up to high temperatures, 450 and 550 °C in air and argon, respectively. This behavior evidences not only the stabilization of this non-equilibrium high-temperature  $\beta$ - $\text{Bi}_2\text{O}_3$  phase at room temperature by this photochemical solution method, but also the high stability of the films with temperature, which enlarges the operation of these materials in practical devices. Additional results reported elsewhere

**Fig. 3** Field-emission gun scanning electron microscopy (FEG-SEM) images and energy dispersive spectroscopy (EDS) analysis of the  $\beta$ - $\text{Bi}_2\text{O}_3$  thin film on a Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrate. **a, b** FEG-SEM surface and cross-section images, respectively. **c** Low magnification FEG-SEM image of the film surface where the EDS analysis has been carried out. EDS maps distribution of the **d** bismuth of the film, **e** oxygen of the  $\beta$ - $\text{Bi}_2\text{O}_3$  film and of the substrate, **f** platinum of the substrate, **g** titanium of the substrate, and **h** silicon of the substrate



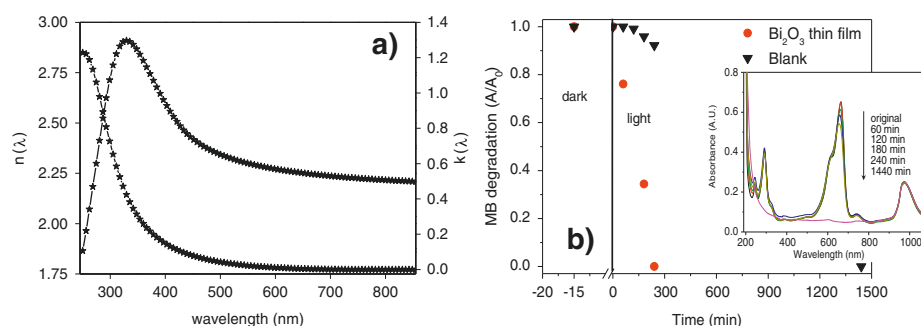
**Fig. 4** Stability with temperature of the  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films deposited from UV-absorbing Bi(III) solutions on Pt-coated silicon substrates. The as-fabricated films show at Room Temperature (RT) the XRD patterns indicated with the label RT. These RT films were subsequently annealed at temperatures between 150 and 850 °C in air [ $\text{P}_{\text{O}_2} \sim 2 \times 10^{-1}$  atm] **a** and **c** or in argon [ $\text{P}_{\text{O}_2} \sim 3 \times 10^{-5}$  atm, measured for films with ZrO<sub>2</sub> based gauge] **b** and **d**



[26, 27] indicate that the UV-irradiated film with the desired  $\beta$ - $\text{Bi}_2\text{O}_3$  phase is stress free, unlike the film prepared without irradiation.

The molecular structure of the bismuth (III)—*N*-methyl-diethanolamine coordination complex has been determined in the literature by single crystal XRD [13],

**Fig. 5** Optical and photocatalytic properties. **a** Refractive index,  $n(\lambda)$ , and extinction coefficient,  $k(\lambda)$ , as a function of the wavelength,  $\lambda$ . **b** Photocatalytic degradation kinetics of methylene blue (MB) over a  $\beta$ - $\text{Bi}_2\text{O}_3$  thin film on Pt-coated Si substrate, for long times, to show how total degradation of the dye is obtained for times below 300 min. The film thickness was  $\sim 50$  nm and the area of  $\sim 2$  cm<sup>2</sup>. The inset shows the photocatalytic degradation of MB alone, without the introduction in the solution of the  $\beta$ - $\text{Bi}_2\text{O}_3$  thin film. The MB only degrades by irradiation for long times of around 1440 min



indicating the formation in this structure of Bi—O bonds with distances in the range of those measured for the  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph [13, 28–33]. Therefore, the initial drying of the deposited layers containing the Bi(III)-*N*-methyl-diethanolamine complex induces the formation of an amorphous —Bi—O—Bi— network with interatomic distances close to those of the tetragonal crystal structure of the  $\beta$ - $\text{Bi}_2\text{O}_3$  polymorph. The further irradiation with UV-light accelerates crystallization [7, 10, 12], producing the straightforward conversion at very low temperatures (from 250 °C, Fig. 2) from the amorphous —Bi—O—Bi—O— cross-linking network to the tetragonal  $\beta$ - $\text{Bi}_2\text{O}_3$  crystal phase. Besides, nanostructured thin films are formed, able of absorbing efficiently the deformation of the substrate and relaxing stresses through the film thickness [26, 27]. As a consequence, the transition from the precursor layers containing this bismuth coordination complex to the  $\beta$ - $\text{Bi}_2\text{O}_3$  crystal phase seems natural and can occur at very low temperature.

Figure 5a shows the optical characteristics of these  $\beta$ - $\text{Bi}_2\text{O}_3$  thin films. These  $\beta$ - $\text{Bi}_2\text{O}_3$  films show light absorption in the visible range. As a consequence, the potential of these nanostructured thin films for the photocatalytic degradation of dyes was studied using MB as pollutant. The photocatalytic degradation of MB over a  $\beta$ - $\text{Bi}_2\text{O}_3$  thin film with an area of  $\sim 2$  cm<sup>2</sup> and a thickness of  $\sim 50$  nm is shown in Fig. 5b. It is observed the degradation of the dye for short times of light exposure. This is an indirect proof of the stabilization of the  $\beta$ - $\text{Bi}_2\text{O}_3$  photocatalyst in these films where the high efficiency of these materials for visible-light photocatalysis [34–38] should be associated to the high purity of the polymorph achieved by the synthesis method here reported.

## 4 Conclusions

The results of this work demonstrate the potential of UV-light to fabricate materials of non-equilibrium crystalline phases. A photochemical synthesis method is successfully applied to the preparation of thin films of the metastable  $\beta$ - $\text{Bi}_2\text{O}_3$  phase from strong UV-absorbing solutions at only 250 °C, far from the formation temperature of this polymorph,  $\sim 650$  °C. The determination of the crystal structure of these films using a X-ray diffractometer equipped with a four circle goniometer undoubtedly shows the formation and stabilization at room temperature of the tetragonal  $\beta$ -polymorph in the films on Pt-coated silicon substrates, without the detection of other  $\text{Bi}_2\text{O}_3$  polymorphs as secondary phases. Besides, these films show a wide temperature stability range. The efficiency of these materials for the photocatalytic degradation of dyes is an indication of the high purity of the  $\beta$ - $\text{Bi}_2\text{O}_3$  phase stabilized in these films.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing financial interests.

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