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Bismuth Oxide Thin Films for Optoelectronic and Humidity Sensing Applications

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Abstract

Bismuth oxide thin films still prove attractive to both scientists and engineers due to their semiconducting behavior, large energy bandgap and high refractive index, despite their often complex structure, both polymorphic and polycrystalline. We present here a summary and a comparison of the morpho-structural and optical properties of such films prepared through three physical vapor deposition (PVD) techniques on several types of substrates kept at different temperatures. Thermal vapor deposition, thermal oxidation in air and pulsed laser deposition are discussed as largely used PVD methods. It is proved that the physical properties of the bismuth oxide thin films can be tailored by changing the substrate nature and its temperature during the deposition process in a way even more relevant than even the chosen deposition method. Thus, bismuth oxide thin films with energy bandgaps ranging from the infrared up to near-ultraviolet can be obtained, depending on their structure and morphology. High refractive index of the films can be also attained for specific spectral ranges. When deposited on certain conductive substrates, the films have much lower electrical resistance and even became sensitive to water vapor. Therefore, humidity sensing and optoelectronic applications of the analyzed bismuth oxide thin films can be easily found and used in both science and technology.

Keywords: bismuth oxide, physical vapor deposition, morpho-structural studies, optical analysis, tailored properties, optoelectronics, humidity sensing

1. Introduction

Most high performance electronic and optoelectronic devices are made of crystalline materials. When drastically reducing the size of crystals up till micrometers and nanometers, their properties change dramatically due to quantum size effects, even completely switching their electrical behavior from metallic to semiconducting, as it is also the case with bismuth. Thus,

thin films, nanowires, nanorods, and nanoparticles became really attractive not only to scientists, but also to engineers due to their specific, distinctive properties, but also because of the need of miniaturization and to material saving.

It is considered that a layer of substance deposited on a support (substrate) is a thin film if it has a thickness ranging between nanometer fractions up to 10 micrometers. Thus, a deposited layer is a thin film if it has a thickness in the order of magnitude or less than the average free path of the electric carriers.

Due to the properties induced by the presence of remote order at crystalline semiconductors, studying the methods of obtaining them as thin films and inferring their properties have taken an extraordinary magnitude. Among thin crystalline semiconductor films, the oxides are intensively studied, the presence of oxygen conferring new, special properties, which recommend them for use in Electronics and Optoelectronics, either for coatings or a single component in different circuits and devices.

Bismuth trioxide thin films, Bi_2O_3, which is the most important industrial compound of bismuth, have also captured the interest of researchers because they have large energy bandgap, high refractive index, high photoconductivity, photosensitivity to ultraviolet radiation, etc. [1–6], properties that recommend bismuth trioxide for a wide variety of applications: optical coatings, solar cells, components in electronic circuitry, recording layers in CDs and DVDs and gas and humidity sensors [7–13]. Moreover, complex oxides containing Bi and V, such as $BiVO_4$ have been found as efficient photoelectrochemical (PEC) material for the treatment of polymer-containing wastewater from oilfields, especially when co-doped with W/Mo [14] or Zn [15] or by adding NaCl to the precursor solution when the chemical bath deposition method was employed for $BiVO_4$ photoanodes [16].

The deposition of thin films is subdivided according to the aggregation state of the depositing material in: (1) solution deposition processes, including the sol-gel technique, electrolysis and spray pyrolysis; (2) deposition from the vapor phase, which is subdivided into: (a) chemical vapor deposition (CVD); (b) physical vapor deposition (PVD).

Physical vapor deposition is a technique used for depositing thin films by condensing atomic or molecular vapor phase species on the surface of a certain substrate. The deposition/coating source is a solid or liquid substance. At a PVD deposition, the material to be deposited is vaporized or sprayed, then it is or it is not mixed with a specific gas, and then it condenses from the vapor state as a thin film onto a substrate facing the material source, the substrate having the anterior surface colder than the flow of deposited material. The deposition is carried out in a vacuum enclosure so that the particles of material to be deposited have a maximum average free path. PVD processes can be divided according to the primary vapor formation method into: (i) vaporization (thermal) processes and (ii) spraying (kinetic) processes, respectively. Several techniques of physical vapor deposition are known, such as: cathodic arc deposition (CAD), sputter deposition, evaporative deposition, electron beam physical vapor deposition (EBPVD) and pulsed laser deposition (PLD), respectively.

The deposition and study of the properties of bismuth trioxide films have been and still are difficult because this oxide presents seven polymorphs [17]: α-Bi_2O_3 (primitive, monoclinic,

stable form), β-Bi_2O_3 (tetragonal, metastable form), γ-Bi_2O_3 (cubic centered, metastable form), δ-Bi_2O_3 (cubic centered, stable form), ϵ-Bi_2O_3 (orthorhombic, metastable), ω-Bi_2O_3 (triclinic, metastable form), and an un-named, metastable form, with cubic primitive structure. Depending on the deposition method and its conditions, on the post-deposition treatment and on the environmental conditions, one or more of bismuth trioxide polymorphs may coexist in the deposited layers. These seven polymorphs have optical and electrical properties that are very different from one another. Thus, the alpha form behaves like a p-type semiconductor at room temperature, passing to n-type conduction around 600°C temperature, depending on the oxygen partial pressure in the surrounding atmosphere [18]. The delta form is among the most efficient ionic conduction oxides, achieved through oxygen vacancies, having a conductivity of about 1 S/cm at 750°C, which is a value with three orders of magnitude larger than the metastable forms of bismuth trioxide, respectively four orders of magnitude greater than the monoclinic alpha form [18, 19].

The deposition of bismuth trioxide can be accomplished by virtually any known method used for thin films: thermal evaporation [11, 20–24]; pulsed laser ablation-PLD [25–30], spray pyrolysis [31–33], electrodeposition [34], sol-gel [35], etc. Depending on the chosen deposition method, on its conditions (nature and temperature of the substrate, the vacuum level, the nature and pressure of the ambient gases, etc.) as well as on the post-deposition thermal treatment, the thin layers of bismuth trioxide deposited up till now have a great variability in terms of structure, morphology and their optical, electrical and other types of physical properties.

Thermal oxidation is a widely used method for the production of oxides of various metals [36–39], including bismuth [9, 21, 22, 40]. Upon thermal oxidation of bismuth, several types of non-stoichiometric oxides (BiO, $Bi_2O_{2.33}$, Bi_4O_7, etc.) can form in addition to Bi_2O_3, whose presence, types of crystalline planes and properties depend on: (i) the properties of the initial bismuth layers; (ii)the oxidation conditions: the maximum attained temperature, the oxidation duration, the heating and cooling rates; (iii) the eventual post-oxidation treatment. There are numerous reports in the scientific literature concerning bismuth oxide thin films obtained by thermal oxidation or by other methods, films exhibiting various structures, morphologies, and optoelectronic properties [1, 9, 21, 40–48]. There are only a few reports on the preparation of bismuth oxide films containing only one type of oxide obtained by thermal oxidation, and these were accomplished at high oxidation temperatures (above 600 K) and/or for long oxidation times of up to a few days, as J. George and collaborators reported [49], along with K. Jayachandran in [22], in both cases the layers consisting of β-Bi_2O_3, while H. A. Zayed obtained polycrystalline δ-Bi_2O_3 thin films [50].

The preparation of bismuth oxide thin films by the PLD (pulsed laser deposition) technique has been rarely used [25–30] because of its relative novelty and of the high cost of the necessary equipment (deposition unit, powerful laser devices, high vacuum, etc.).

The purpose of this chapter is to present three types of physical vapor deposition methods used for the preparation of bismuth oxide thin films with optoelectronic and humidity sensing properties, depending on the set of deposition conditions. A comprehensive methodology for the analysis of the structure, morphology, optical and humidity sensing is also presented together with examples of experimental results and the way the data can and must be interpreted and

further used for practical, scientific and industrial purposes. Thus, this chapter intends to be like a recipe of PVD methods for the preparation of bismuth oxide thin films with tailored properties.

2. Examples of PVD techniques and their corresponding parameters for the preparation of bismuth oxide thin films

As mentioned above, three types of PVD techniques will be discussed here in terms of their most relevant parameters that influence the properties of bismuth oxide thin films. These methods are: (i) thermal vacuum evaporation of bismuth trioxide powder; (ii) thermal oxidation in air of pure bismuth films previously deposited by thermal vacuum evaporation and (iii) pulsed laser deposition of bismuth targets in oxygen atmosphere.

(i) Firstly, classic thermal evaporation in a vacuum can be employed in order to deposit bismuth trioxide thin films, by using high purity Bi_2O_3 (99.999%) as source material, such as the one from Sigma-Aldrich. The depositions have to take place at high vacuum (*e.g.* $8 \cdot 10^{-5}$ *Torr*) onto chemically-cleaned microscope glass substrates (most commonly used, easily available, cheap and resistant to fairly high temperatures) kept at different temperatures, at least 50 degrees apart (*e.g.*27°C = room temperature, RT, 77°C and 127°C, respectively). Such deposition conditions would lead to bismuth trioxide films with a semi-transparent, dark gray appearance [11].

(ii) Alternatively, pure bismuth thin films can be firstly prepared also by thermal evaporation in vacuum (*e.g.* at $5 \cdot 10^{-5}$ *Torr*), onto the same type of microscope glass slides, maintained at different temperatures between room temperature and say 227°C (500 K). After cooling, the bismuth thin films would be submitted to thermal oxidation in air, by means of a home-made device. The oxidation can be performed in two stages of 1 h each, separated by even several days one from the other, such as the properties of the films after the first oxidation stage would not change to air exposure. During the oxidation process, the temperature can be gradually increased up to around 400°C for the first oxidation step and then the temperature should rise at lower temperatures during the second oxidation step (*e.g.* 270°C). The oxidation would be noticed as the films will turn from semi-transparent dark gray as pure bismuth films are, to highly transparent, light yellow-grayish as oxidized layers [23, 24].

(iii) Thirdly, pulsed laser deposition of pure bismuth targets in oxygen atmosphere can also be employed, with and without a radiofrequency discharge of the oxygen inside the high-vacuumed deposition chamber (*e.g.* at $3 \cdot 10^{-5}$ *Torr*). Given the great variability of the types of bismuth oxides that can form and of their properties, depending on the mode and conditions of preparation, it can be chosen to obtain bismuth oxide thin films by the PLD technique by varying: the nature and temperature of the substrate during the depositions, or/and the wavelength (193 or 266 nm) and number of laser pulses (40,000 or 60,000) used for ablation [28–30]. Pure bismuth targets (*e.g.* with 12 mm diameter and 7 mm thickness) can be ablated in a reactive oxygen atmosphere (at *e.g.*: 100 SCCM and 0.6 mbar oxygen partial pressure). An RF source with 13.45 MHz and 150 W can be used for the radio frequency (RF) discharge of the oxygen inside the deposition chamber. Various materials can be employed as substrates at

PLD, from microscope glass slides to silicon, Si (100) or/and Si/Pt, respectively, but the latter proved to give rise to spectacularly different properties of the bismuth oxide films, with electrical resistance up to three orders of magnitude lower than the films deposited on glass and also with a very high sensitivity to humidity as compared to the other prepared films [28]. Substrate heating during the PLD process can also be tried, since this parameter is crucial for the structure, the morphology and the other properties of the deposited films, by controlling the movement, combination, and accumulation of deposing atoms on the substrate. Substrate heating up to even 600°C can be tried and leads to good resulting films.

The thickness of all the deposited and analyzed films can be rather precisely and easily determined by using a Linnik-type of an interference microscope, operated in white light.

The structural analysis of the films can be performed by X-ray Diffractometry (XRD) and/or by transmission electron microscopy (TEM), by means of the SAED (selected area electron diffraction) technique. Thus, typically, an X-ray diffractometer with a Cu Kα (λ = 1.5418 Å) [28, 51] or with a Co Kα target/source (λ = 1.789 Å) [29] can be used. Alternatively, a transmittance electron microscope can be successfully employed for morpho-structural analysis, since it can provide various information about the samples: (i) Bright Field—TEM (BF-TEM) images, (ii) SAED electron diffraction images, with measurements of the radii of the electron diffraction rings through which the interplanar distances can be computed and/or (iii) high-resolution TEM (HRTEM) images from which the interplanar distances can be inferred as well.

The morphology of the films can be analyzed by Scanning Electron Microscopy (SEM) [28, 52, 53] and/or by Atomic Force Microscopy (AFM), the latter with at least 20 nm lateral resolution and 2 nm vertical resolution (*e.g.* a Park XE-100 or a NT-MDT Solver Pro-M AFM [30, 54–57]).

The optical analysis starts by recording the optical transmittance (for the transparent films) and/or reflectance spectra for near-IR, VIS, and near-UV domains, by using a spectrophotometer (*e.g.* type Perkin Elmer Lambda 35), operated at normal incidence, in the air, between at least 200 and 1100 nm. The optical data have to be processed in order to compute the most relevant optical parameters: the refractive index and the absorption coefficient. Then, different models can be applied to these parameters in order to infer new and important figures, such as the energy bandgap and type of electronic transitions within the films [11, 58–61].

Humidity and/or other gas sensing measurements can be performed with a home-made device, made of a closed box kept at room temperature fed with water vapor and a relative humidity meter [28] or a gas and a pressure gauge.

3. Examples of bismuth oxide thin films deposited by the three selected PVD methods: their properties and potential uses

3.1. The structural analysis of bismuth oxide thin films

When thermal vacuum evaporation of Bi_2O_3 powder was employed, most often amorphous films are obtained, independent of the temperature of the glass substrate, as the XRD spectra

proved (see **Figure 1**), by having only one broad maximum instead of individual peaks, like in the case of crystalline samples. The aspect of the XRD spectrum does not change with changing substrate temperature during the depositions.

Instead, when firstly deposing pure Bi thin films onto glass substrates and then thermally oxidize them in open atmosphere, the resulting bismuth oxide films are crystalline, but with very complicated structures. Thus, the oxidized Bi films are most often not only polymorphous but also polycrystalline, and contain not only bismuth trioxide, which is the stoichiometric form of bismuth oxide, but also contain non-stoichiometric bismuth oxides, such as BiO, $Bi_2O_{2.33}$, Bi_4O_7, $Bi_2O_{2.75}$, etc., as they were identified through their specific peaks within the XRD spectrum—see **Figure 2** of such examples. This time, even though the thermal oxidation process is the same for all the pure Bi films, the deposition temperature, t_S of the primary deposited pure Bi films has a decisive influence on the structure of both the primary Bi films, but also on the resulting oxidized films. Thus, as the XRD spectra from **Figure 2** prove, merely
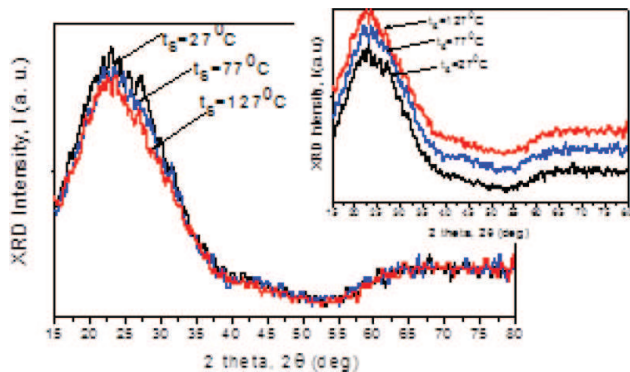

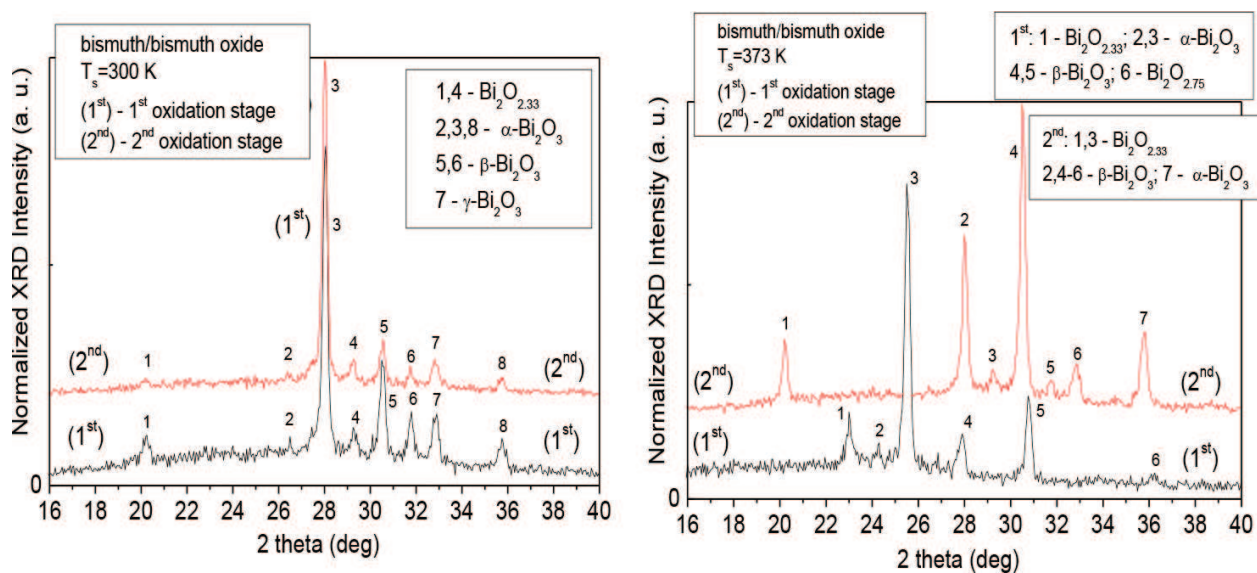**Figure 1.** XRD spectrum for a bismuth trioxide thin film [11].

Figure 2. The XRD spectra of two bismuth oxide thin films obtained by two-stage thermal oxidation of pure bismuth films deposited at two different substrate temperatures [62].
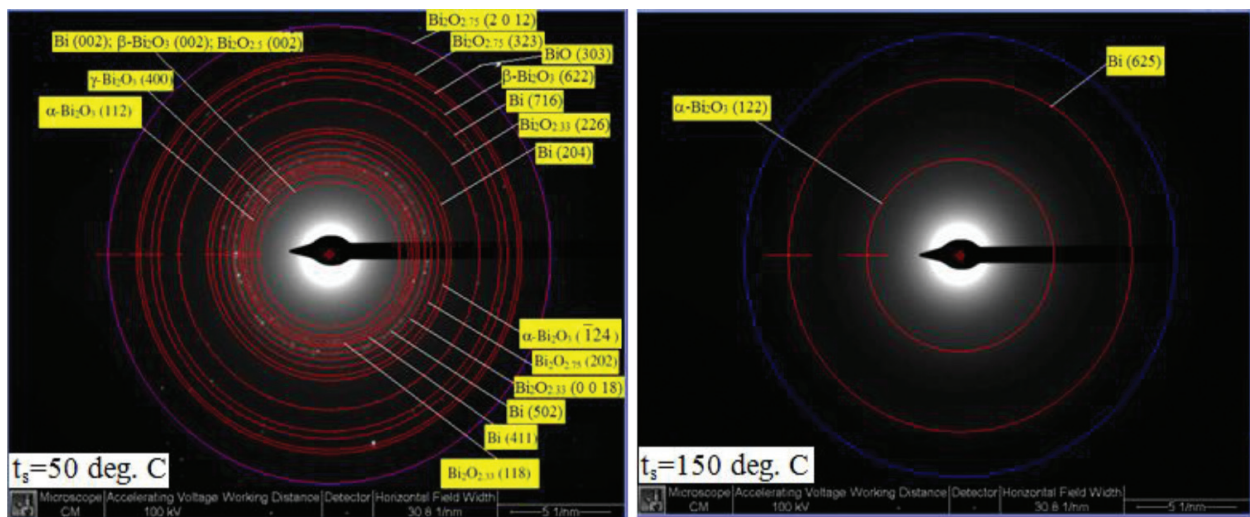
Figure 3. SAED images for two bismuth oxide thin films resulting from the thermal oxidation of pure bi films deposited at different substrate temperatures [63].

changing the substrate temperature with less than 100 degrees makes the thermal oxidation to lead to very different structures. *E.g.* a film deposited at 300 K (27°C) may contain the α, β, γ polymorphs of Bi_2O_3, along with the $Bi_2O_{2.33}$ intermediate oxide, while an oxidized film resulted from a pure Bi layer deposited at 373 K (100°C) may contain only the α and β forms of Bi_2O_3, along with both $Bi_2O_{2.33}$ and $Bi_2O_{2.75}$. The films from **Figure 2** also contain the XRD spectra of the same films after the 2nd oxidation stage (marked with 2nd), showing that further oxidation of the bismuth oxide films changes their structure in a manner and a degree also depending on the substrate temperature during the initial pure bismuth deposition onto the glass. Thus, in the given examples, in the case of a film with $T_s = 300$ K, the 2nd oxidation stage worsens the crystallinity, as the XRD peaks decreases, while for the films with $T_s = 373$ K, the 2nd oxidation eliminates some crystalline planes and gives birth to others instead, with a texturizing change [52].

The SAED technique of TEM provides the most detailed structural analysis of low-dimensional structures. This technique allows one to confirm the complicated structures inferred for bismuth oxide films obtained through thermal oxidation in the air as the XRD study shows. As an example of the application of the SAED technique, the images from **Figure 3** confirm the crucial influence of the substrate temperature, t_s (written in the insets of the electron diffraction images) during the initial pure Bi deposition on the resulting oxidized films.

A 100 degrees temperature difference simplifies the structures drastically, the SAED images passing from a multitude of diffraction rings to only a few [63]. Un-oxidized bismuth is generally present as trapped between the formed oxides in all the types of structural analysis of all the deposited bismuth oxide films, and it will also appear even in the morphological studies, when transversal SEM images are obtained, as it will be pointed out later.

Figure 4 presents an example of an HRTEM image of a bismuth oxide film obtained by the thermal oxidation of pure bismuth film deposited at 227°C. The extremely high magnification of the image (over 1,000,000$\times$) allows for the visualization of the families of crystalline planes—two
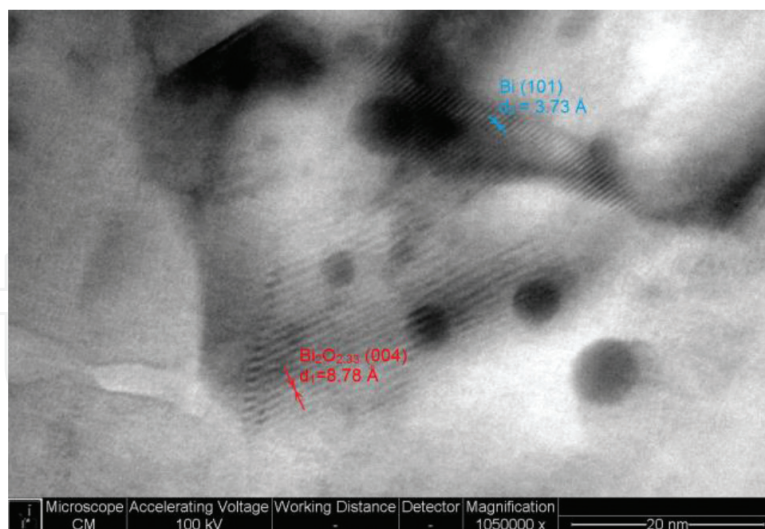
Figure 4. A HRTEM image of a bismuth oxide film with t_S = 227°C.

types in the example: (004) of the non-stoichiometric, seldom found oxide $Bi_2O_{2.33}$, while the others are of the (101) of pure bismuth. The presence of the under-laying and also internally remnant un-oxidized bismuth can be explained by the fact that, as the films are submitted to thermal oxidation, some of the crystalline planes of the forming bismuth oxides block the oxygen access to some bismuth atoms, such the oxidation cannot take place for the entire film.

When using the pulsed laser ablation to prepare bismuth oxide thin films on glass substrates by using pure Bi targets and a reactive oxygen atmosphere (stimulated through a RF discharge), the resulting films still prove to have complicated structures, with remnant un-oxidized bismuth, with intermediate oxides, mixed with different bismuth trioxide polymorphs, as the XRD spectra from **Figure 5** exhibit as examples [29, 56]. Again, the substrate temperature during the deposition process proves critical for the resulting composition and structure of each film, since this parameter controls the mobility of atoms and their mixing and chemical reaction when condensing on the substrates. Moreover, the laser wavelength (namely 266 and 193 nm, respectively) and the number of laser pulses (40,000 or 60,000) used for the ablation of the target also strongly influence the resulting films, as the XRD spectra from **Figure 5** also prove.

Even if the nature of the substrate changes to crystalline silicon, Si (100) or even to Si/Pt, the bismuth oxide thin films prepared by PLD still have complicated structures, as the XRD spectra from **Figure 6** exemplify.

Thus, the films deposited on Si contain both Bi_2O_3 and intermediate oxides [30], along with un-oxidized Bi, while the films deposited on Si/Pt finally reach structural stability, containing merely Bi_2O_3 (*e.g.* β and δ forms) only after thermal treatment (*e.g.* 1-h heating and 1-h cooling) [28]. The substrate temperature, t_S proves important in the case of each type of substrate, even for Si/Pt, the higher t_S (e.g. 600°C as compared to 300°C), the simpler the structure after structural stabilization by post-deposition annealing [28].
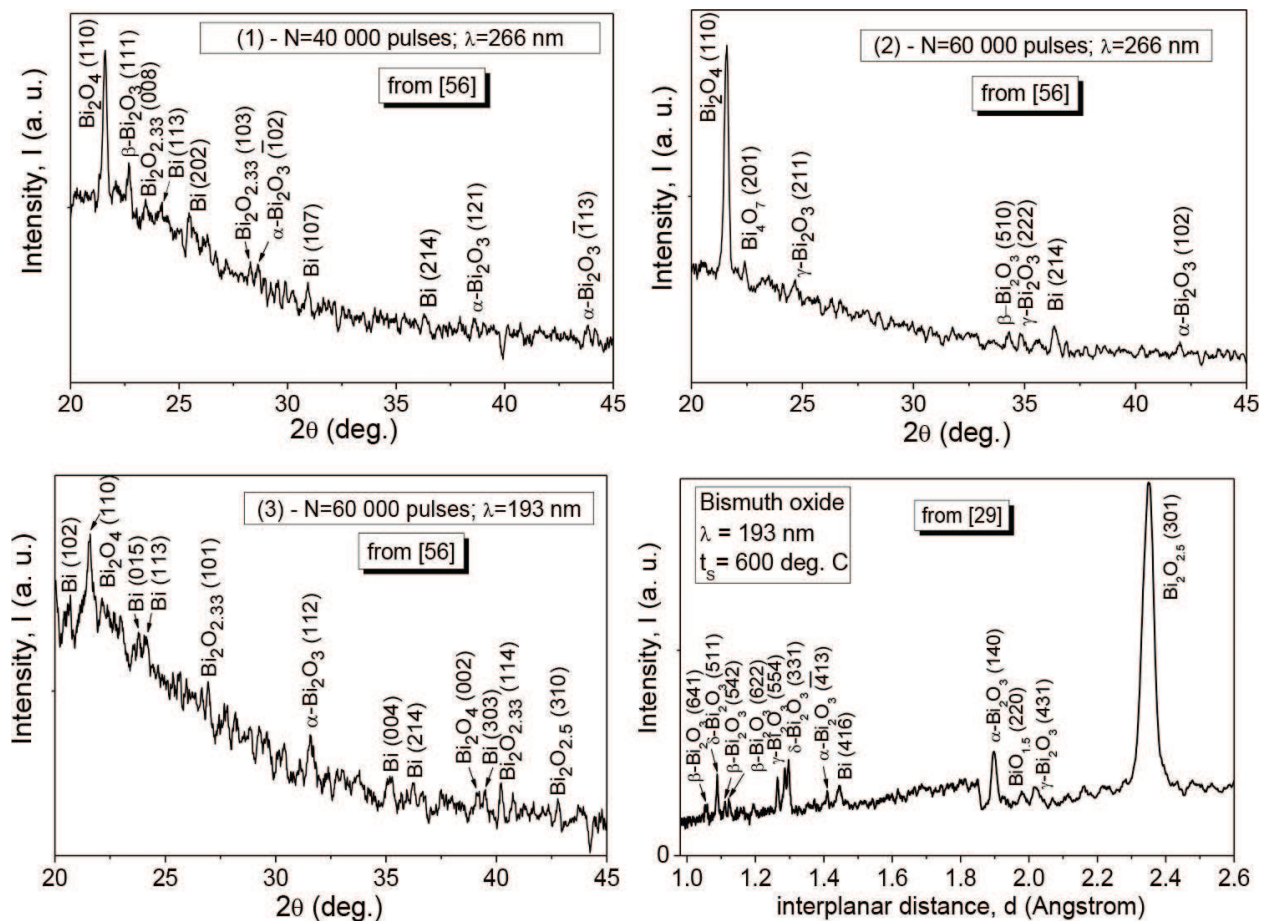
Figure 5. XRD spectra of four bismuth oxide thin films deposited on the glass by RF-PLD, with different deposition conditions [29, 56].

3.2. The morphological analysis of bismuth oxide thin films

Scanning Electron Microscopy can be the choice for the morphological analysis of bismuth oxide thin films. As mentioned above, the remnant bismuth oxide layer underneath the newer formed oxide upon thermal oxidation in air of primary pure Bi films can be also proved by transversal SEM (Scanning Electron Microscopy) images, as the one presented in **Figure 7**.

The normal SEM images as the ones presented in **Figure 8** reveal the morphologies of the bismuth oxide thin films prepared by either method, which are rather uniform when thermal oxidation or PLD are employed on several substrates: glass, Si or Si/Pt.

When using AFM (Atomic Force Microscopy), the aspect of the surface of bismuth oxide thin films is even better revealed as generally having uniformly distributed grains, also sensitive to both the nature of the substrate and to its temperature during the deposition—see **Figures 8** and **9** for such AFM examples. When PLD is used, the grain distribution on the surface of the bismuth oxide film is more uniform, but the grain aspect strongly changes with the wavelength of the UV laser pulses used for the ablation of the bismuth targets, typically 266 and 193 nm.
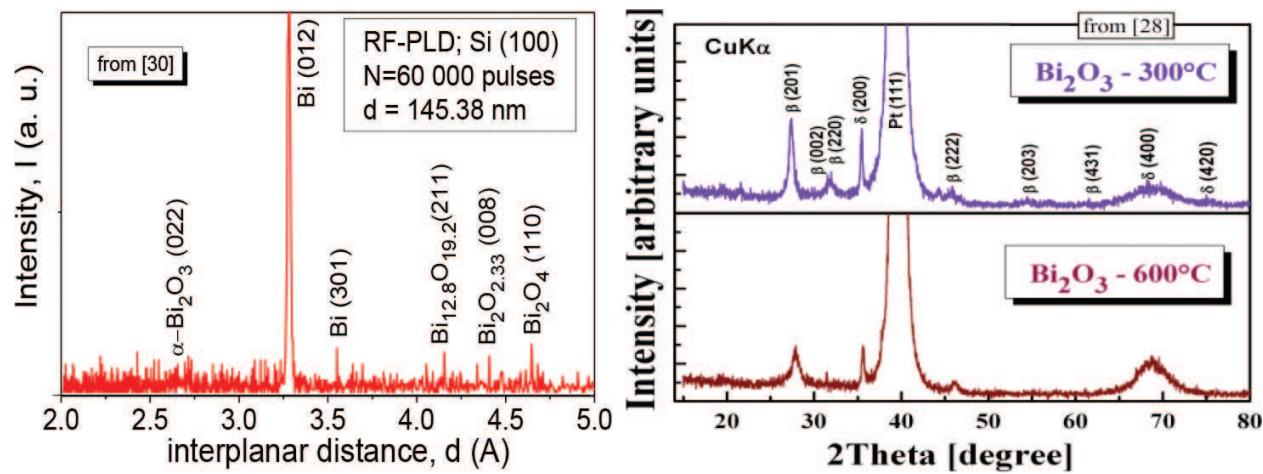
Figure 6. XRD spectra of bismuth oxide thin films deposited by PLD on Si(100) and Si/Pt, respectively [28, 30].
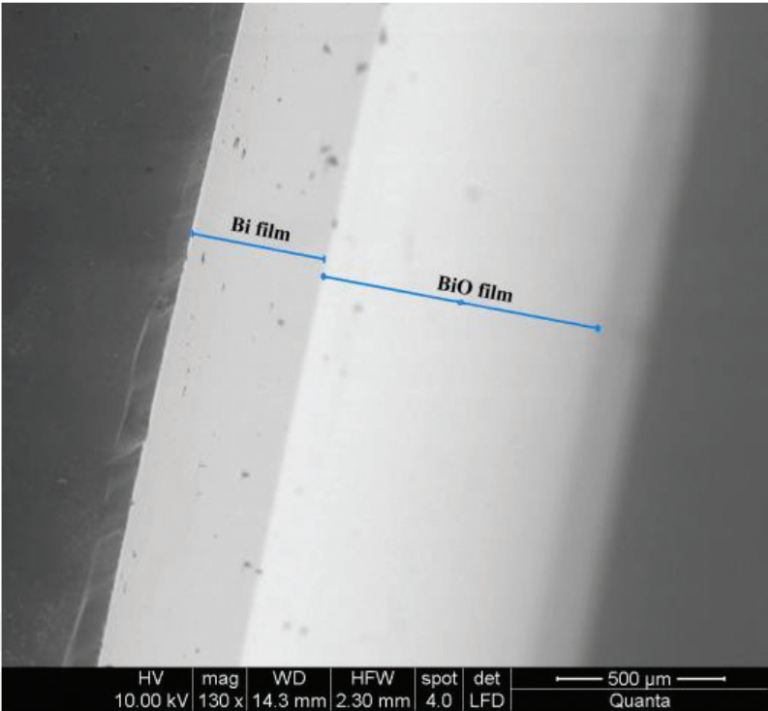

Figure 7. Transversal SEM image of a bismuth oxide thin film prepared by thermal oxidation in air of pure bi films [62].

3.3. Optical analysis of bismuth oxide thin films

The bismuth oxide thin films deposited on glass through each of the three methods described above present high transmittance, either as amorphous or crystalline materials, as the transmittance spectra from **Figure 10** prove. Thus, the transmittance, T of the films surpasses 50% above 400 nm for each of the bismuth oxide film chosen as examples and proofs.

The reflectance of the films presents rather often oscillations with changing wavelength, as **Figure 11** proves.
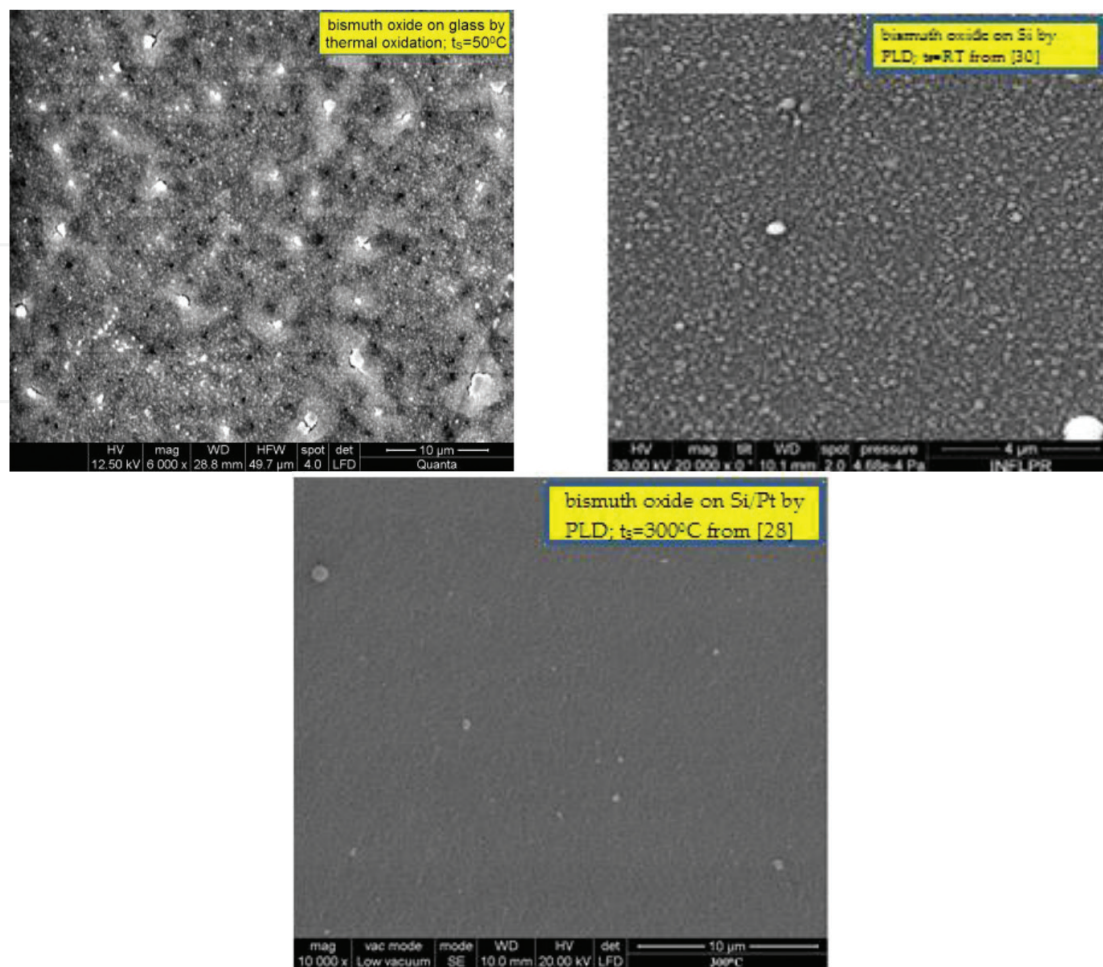
Figure 8. SEM micrographs of bismuth oxide thin films deposited by thermal oxidation (top left image) or by PLD on different substrates (see insets) [28, 30].
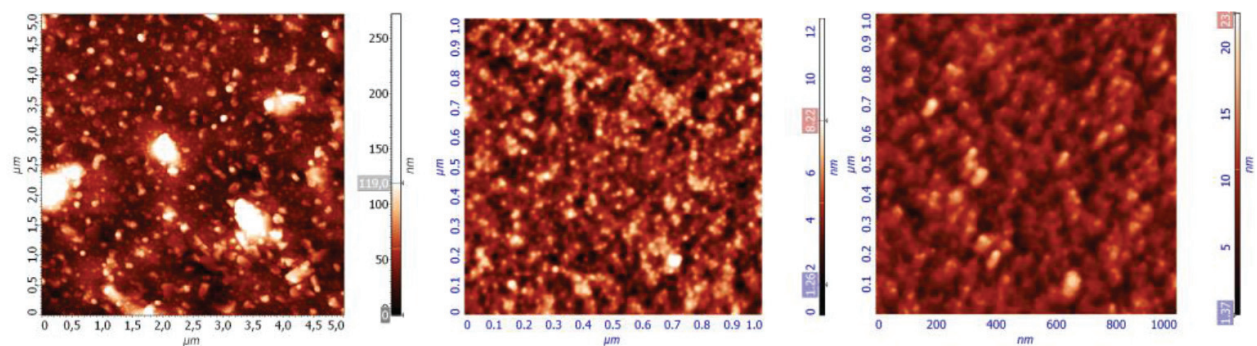

Figure 9. SEM images of bismuth oxide on glass substrates obtained by thermal oxidation (left side image) of by RF-PLD with 266 nm pulses (center image) or with 193 nm pulses (right side image) [55–57].

As the refractive index is concerned, even if its computation is made by taking into account both the reflectance and the transmittance data of the films, its profile or dependence on the wavelength closely follows that of the reflectance data, since it is primarily related to it—see **Figure 12**. Generally, regions with anomalous dispersion can be noticed especially for the
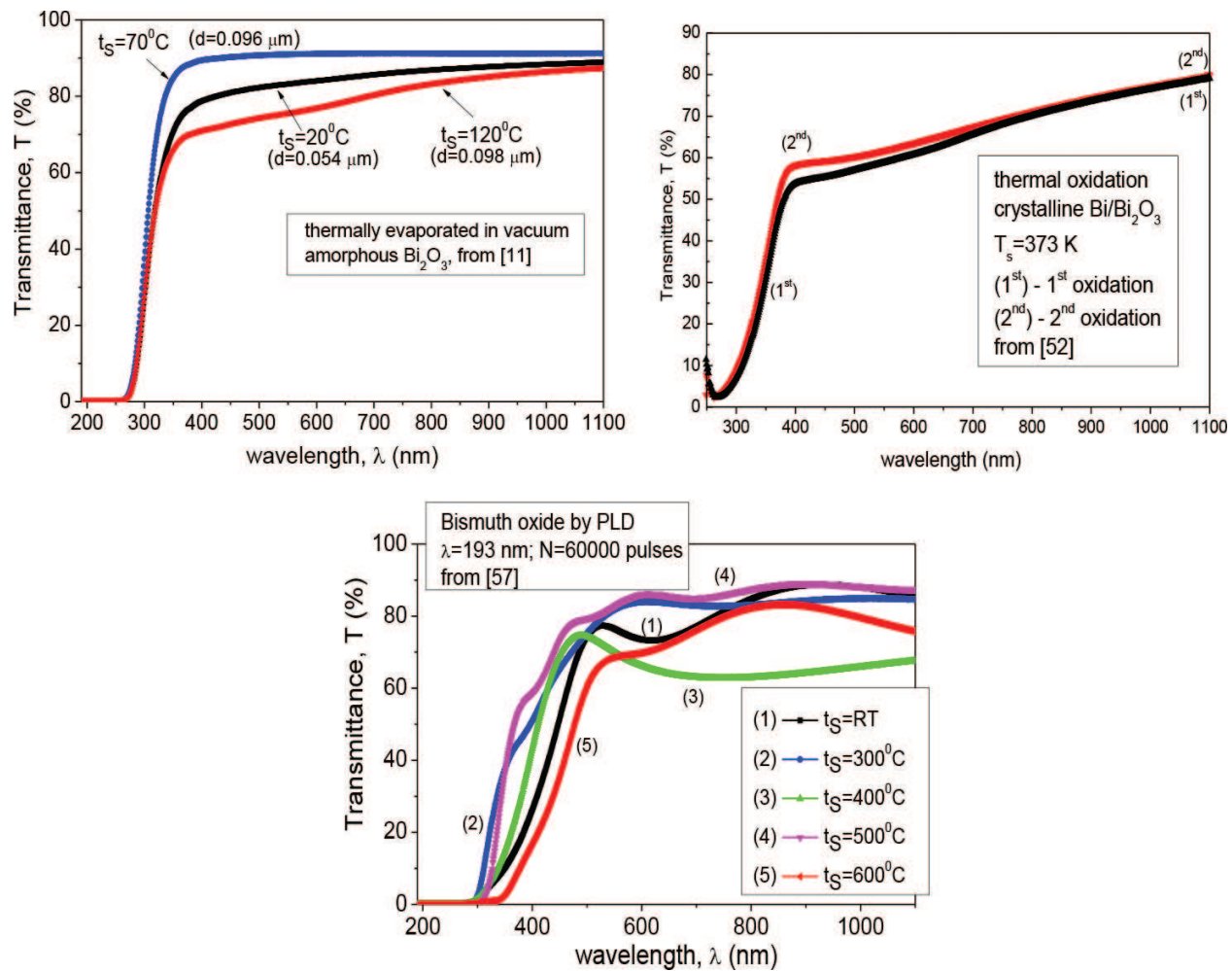
Figure 10. Optical transmission spectra for bismuth oxide thin films prepared by each of the three chosen methods—See insets for details [11, 52, 57].

bismuth oxide films deposited by PLD. Depending on the deposition method and its conditions, the bismuth oxide films can even surpass the value of four for the refractive index.

As for the absorption coefficient, it has to be used for the deduction of the energy bandgap, E_g of the films, according to the model proposed by Tauc [11, 58–61], by plotting $(\alpha \cdot h \cdot v)^r$ in function of the photon energy, $(h \cdot v)$ and by extrapolating the graph to zero, as exemplified in **Figure 13** for amorphous bismuth trioxide deposited on glass by thermal evaporation in vacuum. The values of the 'r' coefficient can be 2, 2/3, 1/2 or 1/3, depending on the type of optical transitions most likely to happen within the analyzed semiconducting films. In the case of the structurally complex bismuth oxide films, indirect-type of optical transitions are the most probably allowed, corresponding to r = 1/2.

Such energy bandgap estimation can be performed for each of the bismuth oxide films for whom optical transmittance data can be obtained (i.e. for transparent films deposited onto transparent substrates), but also by applying the Wemple-Didomenico model for refractive index data as a function of wavelength [11]. Examples of values for the energy bandgap of bismuth oxide thin films prepared by different PVD techniques are given in **Table 1**.
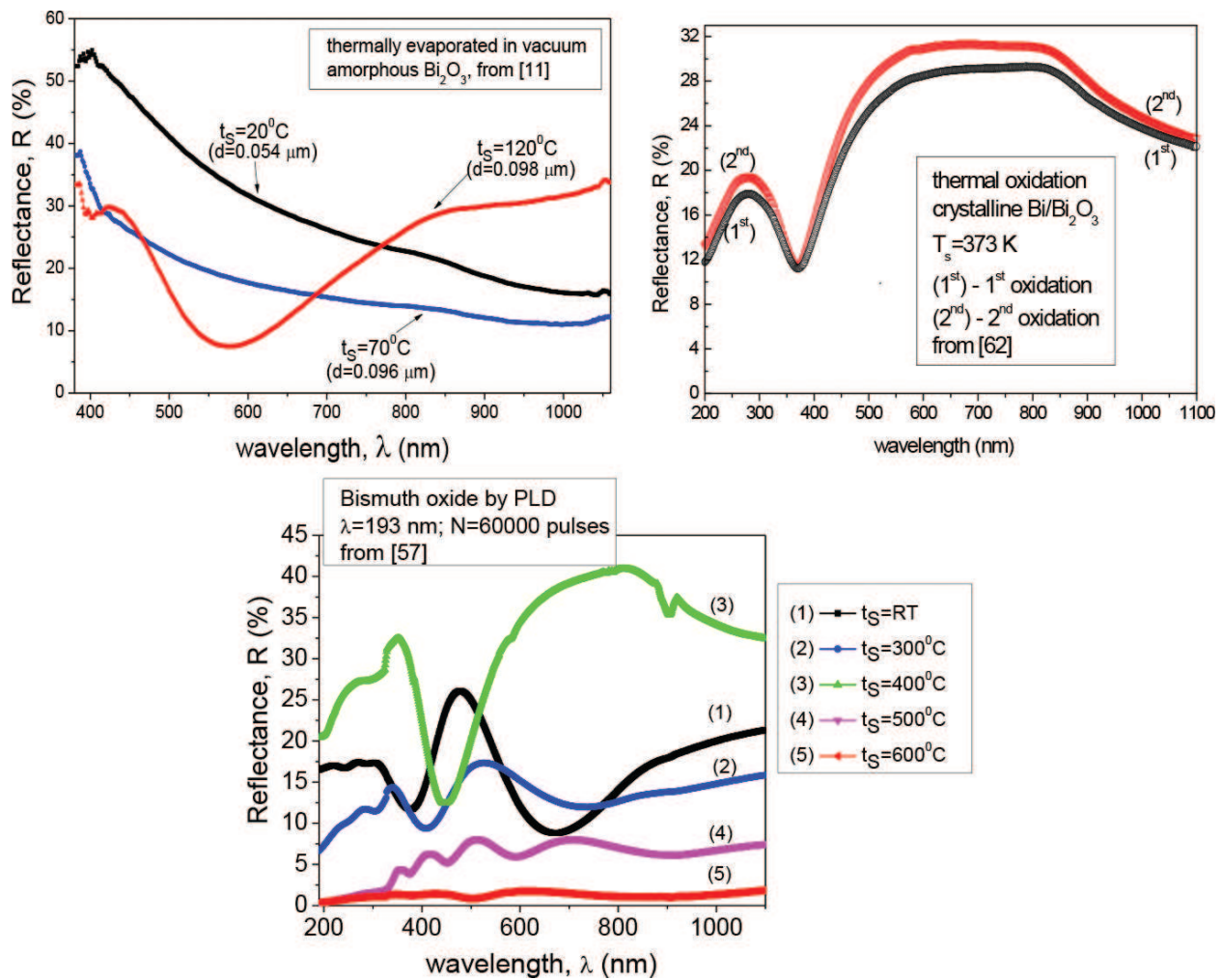
Figure 11. Optical reflectance spectra for bismuth oxide thin films prepared by each of the three chosen methods—See insets for details [11, 51, 62].
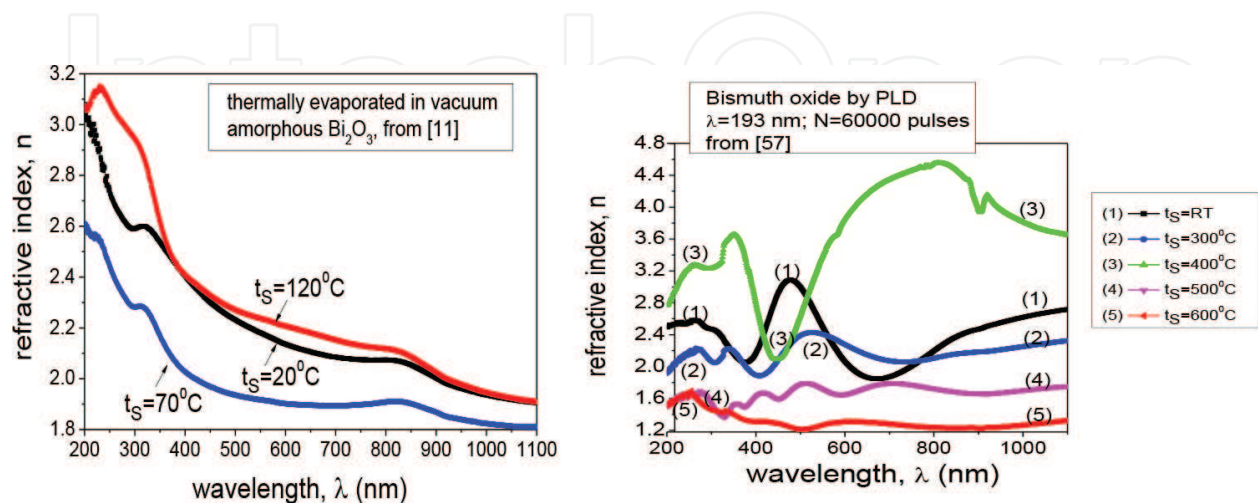

Figure 12. Wavelength dependence of the refractive index for different types of bismuth oxide films [11, 57].
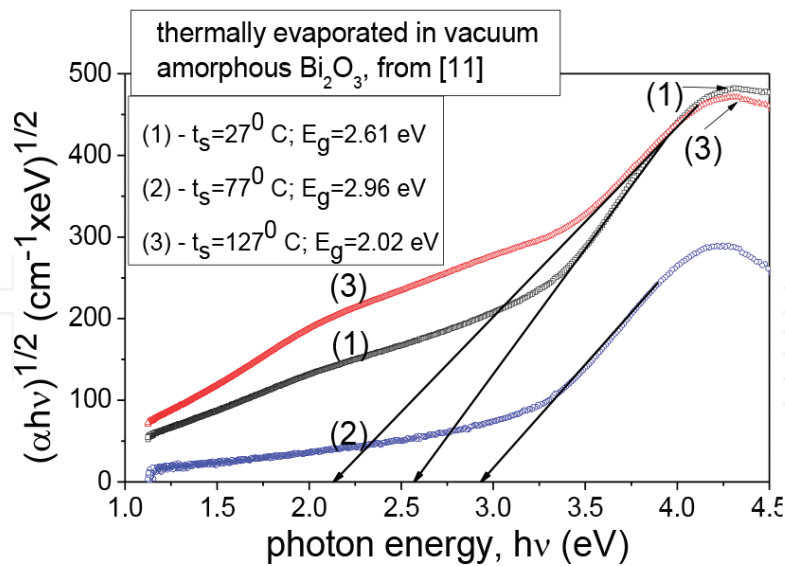
Figure 13. The optical absorption spectra expressed according to Tauc's model, for bismuth trioxide thin films with allowed, indirect transitions and the estimation of their energy bandgaps, E_g [11].

Film preparation method	Substrate temperature, t_S (°C)	Type of optical transition	Optical energy bandgap, E_g (eV)			Reference
Bi thermal oxidation, 1st stage	RT	allowed, indirect $(\alpha \cdot h \cdot v)^{1/2}$	3.01			[51]
	100		1.53*			[54]
	177		2.90			[51]
	200		1.67*			[54]
	227		2.87			[51]
thermal vacuum deposition of Bi_2O_3	RT		2.61			[11]
	77		2.96			
	127		2.02			
PLD on glass, 193 nm, 60,000 pulses	RT	allowed, direct $(\alpha \cdot h \cdot v)^2$	4.15	allowed, indirect	3.30	
	300		4.10		3.55	[29]
	400		4.15		3.25	
	500		3.90		3.35	
	600		4.10		2.75	

Table 1. Energy bandgaps and two types of optical transitions within some bismuth oxide thin films deposited by three PVD methods; * E_g inferred through the Wemple-Didomenico model [11, 52, 54, 57].

3.4. Testing the humidity sensitivity of bismuth oxide thin films

Most often, the electrical resistance measurements of bismuth oxide films deposited onto glass and silicon substrates have extremely high resistances, of Gigaohms and more, as in the case of the three PVD methods exemplified here. Still, the films deposited onto conductive substrates, such as Si/Pt exhibit merely Megaohms resistances, which allows for testing their sensitivity to
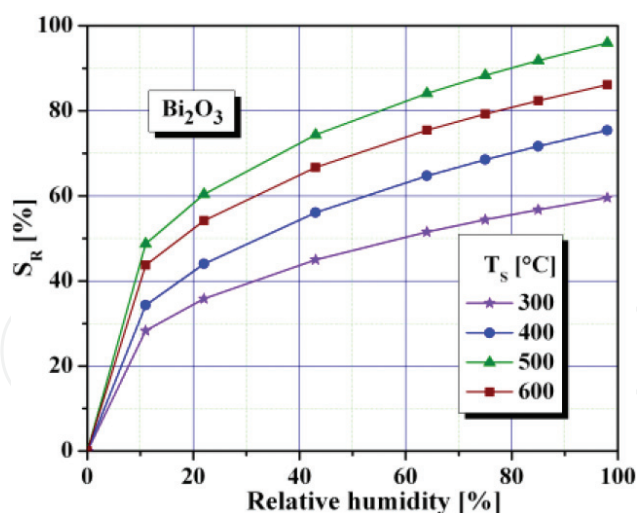
Figure 14. Change of the relative variation of the electrical resistance of bismuth oxide thin films deposited by PLD on Si/Pt substrates, maintained at different temperatures [28].

humidity and/or other gases. As **Figure 14** exemplifies, bismuth oxide thin films deposited by PLD on Si/Pt present excellent sensitivity to increasing humidity, which recommends them for atmospheric sensors [28]. Thus, as the relative humidity increases, the electrical resistance of such films strongly increases, up to 100% relative variation. This behavior is given by the oxygen affinity of metal oxides thin films which can uptake oxygen atoms from the atmosphere in the pores of the structures, linking to the free metal atoms and also because, generally, metal oxide films are oxygen defectives and, thus, need oxygen for stoichiometry. Again, the substrate temperature during the depositions has a relevant influence even on the humidity sensitivity of the films. In the case of the examples from **Figure 14**, the film deposited at 500°C has the highest sensitivity to relative humidity.

4. Conclusions

Bismuth oxide thin films represent both an attraction and a challenge for scientists in terms of their properties depending on their often complicated structure. Different PVD methods can be used to prepare such films, each method having its specific advantages and disadvantages related to the technique itself, but also to the implied costs of needed devices.

This chapter presented a comparison between the structures, morphologies, optical and humidity sensing properties of bismuth oxide thin films prepared by three PVD methods: thermal vacuum evaporation of bismuth trioxide powder, thermal oxidation in air of pure bismuth films previously prepared by thermal evaporation in vacuum, and pulse laser deposition of pure bismuth targets in oxygen atmosphere.

Generally, polymorphic and polycrystalline bismuth oxide films are obtained by using pure bismuth as starting material and then thermal oxidation or PLD in oxygen atmosphere are employed. Thus, mixtures of Bi_2O_3 polymorphs (α, β, γ and δ - most often) along with several

non-stoichiometric oxides ($Bi_2O_{2.33}$—most encountered) are more likely to be obtained. The structure, morphology, optical properties and humidity sensing properties of the bismuth oxide films depend on the nature and temperature of the substrate during the primary deposition much stronger than on the chosen deposition method. Thus, the films deposited onto conductive substrates, such as Si/Pt present much lower electrical resistance than those deposited onto typical substrates such as glass or silicon. Humidity or even other gas sensing cannot be tested for films with high electrical resistance since the resistance variation with gas concentration would not be significant or even measurable.

Generally, bismuth oxide thin films prove to have high optical transmittance and rather high refractive index, along with a semiconducting behavior and a large energy bandgap, properties recommending them to Optoelectronics, especially since these properties can be tailored by properly changing the deposition method and especially the nature and temperature of the substrate.

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