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1 **Correlation between structural and optical properties of WO<sub>3</sub> thin films sputter**  
2 **deposited by glancing angle deposition**

3  
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## 11 **Abstract**

12 Tungsten oxide  $\text{WO}_3$  thin films are prepared by dc reactive sputtering. The GLancing Angle  
13 Deposition method (GLAD) is implemented to produce inclined columnar structures. The incident  
14 angle  $\alpha$  between the particle flux and the normal to the substrate is systematically changed from 0  
15 to  $80^\circ$ . For incident angles higher than  $50^\circ$ , a typical inclined columnar architecture is clearly  
16 produced with column angles  $\beta$  well correlated with the incident angle  $\alpha$  according to conventional  
17 relationships determined from geometrical models. For each film, the refractive index and  
18 extinction coefficient are calculated from optical transmittance spectra of the films measured in the  
19 visible region. The refractive index at 589 nm drops from  $n_{589} = 2.18$  down to 1.90 as  $\alpha$  rises from 0  
20 to  $80^\circ$ , whereas the extinction coefficient reaches  $k_{589} = 4.27 \times 10^{-3}$  for an incident angle  $\alpha = 80^\circ$ ,  
21 which indicates that the films produced at a grazing incident angle become more absorbent. Such  
22 changes of the optical behaviours are correlated with changes of the microstructure, especially a  
23 porous architecture, which is favoured for incident angles higher than  $50^\circ$ . Optical band gap  $E_g$ ,  
24 Urbach energy  $E_u$  and birefringence  $\Delta n_{617}$ , determined from optical transmittance measurements,  
25 are also influenced by the orientation of the columns and their trend are discussed taking into  
26 account the disorder produced by the inclined particle flux.

27

## 28 **Keywords**

29  $\text{WO}_3$  films, GLAD, inclined columns, refractive index, porosity, optical band gap, Urbach energy,  
30 birefringence.

## 31 **1. Introduction**

32 Transition metal oxides represent a very attracting class of materials because of the wide range of  
33 physical and chemical properties that they exhibit. Among these oxide compounds, tungsten oxide  
34 thin films have been extensively investigated due to their important applications as active layers for  
35 electrochromic window devices [1-4], sensors for toxic gases [5-8], optical coatings with high  
36 refractive index [9, 10] or transparent and low resistive oxide materials [11, 12]. It is well known  
37 that many chemical and physical characteristics of metal oxide thin films are strongly connected to  
38 their chemical composition, especially the oxygen-to-metallic concentrations ratio, which can be  
39 tuned in order to get a metallic, semi-conducting or insulating behaviour according to the metalloid  
40 content in the film [13-16]. However, playing with the chemical composition is not the only  
41 approach to tune the properties of metal oxide thin films. The structure at the sub-micrometric scale  
42 can also influence the film performances for many applications [17]. So, the design and the growth  
43 control of nanostructures in thin layers appear as important issues, e.g. in order to control the optical  
44 properties by playing on structural features. To this aim, various strategies have been proposed for  
45 the structuration of thin films [18].

46 In the last decade, the interest of nanostructuring by evaporation and/or sputtering techniques was  
47 particularly boosted by the GLancing Angle Deposition (GLAD) method [19]. This method is based  
48 on the preparation of thin films on fixed or mobile substrate, with an oblique incidence of the  
49 incoming particle flux. Indeed, when the atomic vapour flow comes up at a non normal incident  
50 angle  $\alpha$ , the nucleation sites intercept the flow of particles. This creates a shadowing effect and  
51 there is a tilted grain growth of columnar shape leading to inclined columnar structures with an  
52 angle  $\beta$  with respect to the normal of the substrate surface. Nature, crystallography, temperature and  
53 surface conditions of the substrate, energy and interactions of the condensed particles with the  
54 substrate, among other parameters, have a decisive role in the growth mode of the coating. As a  
55 result, the GLAD technique can control the structure of thin films at the micro- and nanoscales. The  
56 experimental setup has two degrees of freedom: a rotation axis at an angle  $\alpha$ , which allows to vary

57 the incident angle of the particle flux, and a rotary axis at an angle  $\phi$  (also called azimuth angle),  
58 which modifies in an indirect way, the position of the particle source. The produced architectures  
59 can be of type i) columnar and inclined; ii) chevron or zigzag by alternating periodically the  
60 incident angle of particles from  $+\alpha$  to  $-\alpha$  maintaining constant  $\phi$  angle (azimuthal angle around the  
61 substrate) or with a  $180^\circ$  rotation of  $\phi$  keeping constant  $\alpha$  angle; iii) spiral or helical thanks to a  
62 continuous rotation of  $\phi$  at a constant incident angle  $\alpha$ . This latter type adds to the potential of the  
63 GLAD technique. Moreover, changing wisely  $\alpha$  and  $\phi$  angles as well as speeds of rotation, more  
64 original structures can be obtained such as porous columnar structures with variable diameters [20]  
65 or helical columns with squared sections [21]. In the end, the GLAD technique exploits the effects  
66 of shadowing created by a tilted substrate relative to normal incidence and a change of the direction  
67 of the particle flux through a rotation of the same substrate during the deposition. The two  
68 combined can generate different forms of columns and varied architectures. For example, Robbie et  
69 al. [22, 23] or Van Popta et al. [24] have deposited by evaporation some structured films with  
70 columnar architectures showing sinusoidal, helical and more complex forms. This variety allows  
71 envisaging applications in many fields such as biomedical system [25], photonic devices [26],  
72 microsensors [27], etc. Moreover thin films deposited by GLAD have high porosity and anisotropic  
73 behaviours, which can be used as rugate filters [28], wavelength-selective polarizer [29], or  
74 antireflection coating [30].

75 The purpose of this article is to study the structural and optical properties of the sputter deposited  
76 tungsten oxide  $\text{WO}_3$  nanostructured thin films grown using various incident angles  $\alpha$  of the particle  
77 flux from  $0$  to  $80^\circ$ . We systematically investigate how the structure and optical properties  
78 (refractive index, extinction and absorption coefficients, optical band gap, birefringence) of such  
79 oriented thin films can be tuned by changing the incident angle of the sputtered particles. The  
80 evolution of the porous structure connected to the columnar orientation is especially analyzed in  
81 order to discuss and understand some relationships between the architecture of the films and their  
82 resulting optical behaviours.

83

## 84 **2. Experimental details**

85 WO<sub>3</sub> films were sputter deposited by DC reactive magnetron sputtering using a home made system  
86 [31, 32]. A tungsten target (5 cm diameter with purity 99.9 at. %) was powered at a constant current  
87 density  $J = 25.5 \text{ A.m}^{-2}$ , with an argon partial pressure  $P_{Ar} = 0.1 \text{ Pa}$  and an oxygen partial pressure  
88  $P_{O_2} = 0.08 \text{ Pa}$ . Substrates (grounded and kept at room temperature) were glass plates and (100)  
89 silicon wafers. The distance between the target and the substrate was fixed at 60 mm. The growth of  
90 the films was stopped at a thickness close to 1  $\mu\text{m}$  thanks to the calibration of the deposition rate. A  
91 systematic change of the incident angle from  $\alpha = 0$  to  $80^\circ$  with a  $10^\circ$  increment was performed to  
92 tune the inclined columnar structure. Films deposited on glass substrates were characterized thanks  
93 to optical transmittance spectra measured with a Lambda 900 Perkin Elmer spectrophotometer in  
94 the visible range from 1.55 to 3.10 eV (i.e. wavelength in-between 800 to 400 nm). Refractive  
95 index, extinction coefficient and absorption coefficient were determined from interference fringes  
96 obtained with experimental optical transmittance spectra using Swanepoel's method [32]. Films  
97 prepared on (100) silicon wafers were cross-sectioned and observed by field effect scanning  
98 electron microscopy (SEM) using a JEOL 6400 F. WO<sub>3</sub> structures were also characterized by X-ray  
99 diffraction (XRD). Measurements were carried out using a Bruker D8 focus diffractometer with a  
100 cobalt X-ray tube ( $\text{Co } \lambda_{K\alpha} = 1.78897 \text{ \AA}$ ) in a  $\theta/2\theta$  configuration.

101

## 102 **3. Results and discussion**

### 103 **3.1 Structural characterization**

104 Tungsten oxide thin films prepared with an incident angle  $\alpha$  lower than  $50^\circ$  do not exhibit a clear  
105 inclined columnar structure. A densely packed feature is rather observed with a smooth surface  
106 topography. However, a further increase of the incident angle ( $\alpha$  higher than  $50^\circ$ ) leads to a rougher  
107 film/air interface and a more defined columnar growth. Observations by SEM of surfaces and cross-  
108 sections of WO<sub>3</sub> thin films sputter deposited with an incident angle  $\alpha$  of  $70$  and  $80^\circ$  are shown in

109 figure 1. It is worth of noting that the top of the columns has a rather sharp appearance (Fig. 1a),  
110 which is even more emphasized for  $\alpha = 80^\circ$  (surface state becomes irregular and more voided as  
111 illustrated in figure 1c). Such increase of the surface roughness versus incident angle of the  
112 sputtered particles is in agreement with previous investigations focused on metal oxide coatings  
113 produced by GLAD [33, 34]. It is mainly attributed to the shadowing effect at the atomic scale,  
114 which prevails over the surface diffusion of adatoms as the incident angle rises. The structural  
115 anisotropy (formation of growth islands connected to each other by chains perpendicular to the  
116 plane of incidence) previously claimed by Tait et al. [35], is slightly marked for sputtered tungsten  
117 oxide films. The top of the columns appears more or less connected to each other according to the x  
118 direction and perpendicular to the particle flux (Fig. 1a and 1c).

119 Inspection of the cross-sectional view ensures that the GLAD  $\text{WO}_3$  films are composed of slanted  
120 columns and inter-columnar voids (Fig. 1b and 1d). The columns are inclined towards the direction  
121 of the incoming vapour flux. The column angle  $\beta$ , defined as the angle between the substrate surface  
122 normal and the long axis of the slanted columns, is measured from the cross-section SEM images.  
123 For incident angle  $\alpha$  lower than  $50^\circ$ , the column angle  $\beta$  can not be accurately determined since no  
124 clear columnar growth has been produced but a densely packed structure. For higher angles of  
125 incidence ( $\alpha > 50^\circ$ ), SEM images exhibit morphologies composed by columns and inter-columnar  
126 gaps. The columns become increasingly separated and can easily be distinguished at an incident  
127 angle  $\alpha$  of  $70^\circ$  and even more at  $80^\circ$ . The resulting column angles  $\beta$  are  $50$  and  $54^\circ$  for incident  
128 angles  $\alpha$  of  $70$  and  $80^\circ$ , respectively. Such column angles deviate from the empirical tangent rule  
129 [36], which predicts  $53$  and  $70^\circ$ , respectively. This rule provides a first order approximation of the  
130 expected  $\beta$  angles. Since the growth can be disturbed by many parameters (temperature, particle  
131 energy, pressure), the tangent rule fails to well describe experimental column angles, especially for  
132 grazing incident angles. This is indeed relevant for thin films deposited by the sputtering process,  
133 where column angles are often lower than those calculated with various ballistic rules [37, 38].  
134 However, our produced  $\text{WO}_3$  column angles are in good agreement with relationships proposed by

135 Tait et al. [39]. The sputtering pressure required to maintain the glow discharge restricts the mean  
136 free path of the sputtered particles and thus, reduces the shadowing effect. As a result, the  
137 theoretical column inclinations predicted by the simple tangent rule is systematically overestimated.  
138 Since tungsten oxide thin films have been deposited at room temperature (substrate temperature is  
139 lower than 0.3 times the melting point of  $\text{WO}_3$  compound), one could expect a poorly crystallized  
140 material. However, XRD analyses exhibit diffracted signals (Fig. 2). Peaks corresponding to the  
141  $\text{WO}_3$  monoclinic structure are clearly identified for incident angles included between  $\alpha = 0$  and  $80^\circ$ .  
142 For normal incidence ( $\alpha = 0^\circ$ ), as-deposited films are weakly crystallized since the major diffracted  
143 peaks exhibit low intensity and the average crystallite size calculated from the Scherrer equation is  
144 smaller than 15 nm. An increase of the incident angle  $\alpha$  up to  $40^\circ$  leads to more intense peaks for all  
145 crystallographic planes, without any preferential orientation. In addition, the crystallite size reaches  
146 30 nm for  $\alpha = 40^\circ$  and the diffracted patterns (peaks position, intensity or full-width-at-half-  
147 maximum) do not evolve as the incident angle  $\alpha$  increases up to  $80^\circ$ . This improved crystallinity as  
148 a function of the incident angle has also been observed for other ceramic thin films produced by  
149 GLAD [40, 41]. In addition, a reverse effect has been observed by others for some materials [42],  
150 showing a reduction of the long range order up to an amorphous structure as the incident angle  $\alpha$   
151 rises. As a result, the dependence of crystallinity on the deposition angle has to be considered on a  
152 case by case basis and still remains an open question. Nevertheless, it can be correlated with the  
153 surface diffusion phenomenon of the sputtered particles. This phenomenon preferentially takes  
154 place in the direction of the particle flux, particularly for grazing incident angles. During initial  
155 growth and as the incident angle  $\alpha$  increases, the formed islands start collecting more adatoms.  
156 They will grow faster and tend to capture more incoming vapour flux, reinforcing the growth of  
157 large crystallites at the expense of other grains that are consumed during the process. This possible  
158 explanation of the long range crystalline order is in agreement with the increase of the crystallite  
159 size reported from XRD measurements since grain size rises from 15 to 30 nm as the incident angle  
160  $\alpha$  changes from 0 to  $40^\circ$ , and finally  $80^\circ$ .



161

## 162 **3.2 Optical characterization**

163 Optical transmittance spectra of tungsten oxide films deposited on glass substrates have been  
164 measured in the visible region for various incident angles  $\alpha$  of the particle flux (Fig. 3). As expected  
165 for  $\text{WO}_3$  compound, typical interference fringes are observed. The films deposited by conventional  
166 process ( $\alpha = 0^\circ$ ) exhibit the highest amplitudes. For a given wavelength (e.g. 600 nm) the envelop  
167 curve is below 70 % for the minimum of transmittance ( $T_{min}$ ), whereas it is higher than 91 % for the  
168 maximum of transmittance ( $T_{Max}$ ). Amplitude of the fringes is slightly reduced up to an increasing  
169 incident angle  $\alpha = 40^\circ$ . The amplitudes reduction becomes more significant for grazing incident  
170 angles, especially for  $\alpha = 80^\circ$  since  $T_{min}$  is close to 77 % and  $T_{Max}$  is 88 % at 600 nm. For this high  
171 incident angle of  $80^\circ$ , it is also worth of noting that fringes tend to disappear as the wavelength  
172 comes closer to the absorption edge (i.e. between 400 and 500 nm), which can be attributed to the  
173 enhancement of the light diffusion. This later is not solely due to structural modification in the film  
174 (columns are more inclined), but it also comes from an increased surface roughness for incident  
175 angles higher than  $40^\circ$ , as previously observed from SEM analyses (Fig. 1) and in agreement with  
176 other theoretical and experimental investigations [43].

177 From optical transmittance measurements of the  $\text{WO}_3$  films deposited on glass substrate, refractive  
178 index  $n$  (Fig. 4) and extinction coefficient  $k$  (Fig. 5) have been calculated as a function of the  
179 wavelength in the visible region using the Swanepoel's method [44]. The refractive index and  
180 extinction coefficient dispersion curves of  $\text{WO}_3$  films deposited at various incident angles are all  
181 fitted by using the Cauchy dispersion equation in the range of wavelengths 400 to 800 nm. Both the  
182 optical index and extinction coefficient follow the Cauchy dispersion evolution as a function of  
183 wavelength for any incident angle of the particle flux.  $\text{WO}_3$  thin films prepared with a normal  
184 incidence of the particle flux ( $\alpha = 0^\circ$ ) exhibit the highest refractive index together with the lowest  
185 extinction coefficient. For a reference wavelength of 589 nm,  $n_{589} = 2.17$  (and  $k_{589}$  is below  $1.42 \times 10^{-3}$ ).  
186 <sup>3</sup>). This value is below that of the bulk  $\text{WO}_3$  material since  $n_{bulk} = 2.50$  for the same given

187 wavelength [45]. It shows that the films sputter deposited at normal incidence are quite compact but  
188 nonetheless contain significant amounts of defects and voids.

189 A systematic change of the incident angle of the particle flux from 0 to 80° leads to a clear decrease  
190 of the refractive index of tungsten oxide thin films from  $n_{589} = 2.17$  down to 1.90, respectively. This  
191 drop becomes very significant when the incident angle is higher than 40°. This effect has already  
192 been observed for other metallic oxide thin films prepared by GLAD [46-48]. It is mainly ascribed  
193 to the growth of a more porous structure versus incident angle. In evaporation or sputtering  
194 processes, the deposited film's planar density is determined by the shadow length and thus, can be  
195 tuned by the incident angle  $\alpha$ . Varying the amount of bulk material in the film is a way to change its  
196 refractive index.

197 Similarly, extinction coefficient is nearly constant close to  $1.50 \times 10^{-3}$  at 589 nm up to an incident  
198 angle of 60°. Hence, it remains close to values corresponding to typical dielectric and transparent  
199 compounds. However, for an incident angle of 80° where  $k_{589}$  is higher than  $4.27 \times 10^{-3}$ . Such  
200 increase of the extinction coefficient correlates with the increase of the surface roughness  
201 commonly measured for high incident angles. Indeed, the low values of  $k$  in the visible region is a  
202 qualitative indication of the good surface smoothness of thin films [49]. Furthermore, the high  $k$   
203 value obtained for  $\alpha = 80^\circ$  suggests the presence of marked inhomogeneities in the films (defects,  
204 disordering, oxygen vacancies, surface corrugation), especially a rougher film/air interface favoured  
205 for high glancing angles of deposition.

206 The packing density  $p$  and, hence, the porosity  $\pi$  of the  $\text{WO}_3$  GLAD films ( $\pi = 1 - p$ ) are significant  
207 characteristics of sputter deposited materials. They can be calculated based on the effective media  
208 approximation, and thus using the mixture rule proposed by Bruggemann [50]:

$$209 \quad \chi_a \left( \frac{\epsilon_a - \epsilon_{eff}}{\epsilon_a + 2 \times \epsilon_{eff}} \right) + \chi_b \left( \frac{\epsilon_b - \epsilon_{eff}}{\epsilon_b + 2 \times \epsilon_{eff}} \right) = 0 \quad (1)$$

210 Where  $a$  and  $b$  components are randomly distributed in space with volume fractions of  $\chi_a$  and  $\chi_b$ ,  
211 respectively ( $\chi_a + \chi_b = 1$ ). The dielectric properties of the medium are described by an effective

212 permittivity  $\epsilon_{eff}$ , and that of  $a$  and  $b$  components are  $\epsilon_a$  and  $\epsilon_b$ , respectively. For our films, we  
213 considered that  $a$  component is the  $WO_3$  bulk material and  $b$  component is the vacuum. As a result,  
214  $\epsilon_{eff}$  is the permittivity of the film. Assuming that the bulk tungsten trioxide compound has a  
215 refractive index of  $n_b = 2.50$  at 589 nm [45] and from the refractive index of the film  $n_f$  at 589 nm,  
216 packing density and so, porosity have systematically been calculated and compared to the refractive  
217 index as a function of the incident angle  $\alpha$  (Fig. 6). Refractive index and porosity exhibit a reverse  
218 evolution as the incident angle  $\alpha$  rises.  $WO_3$  films deposited by conventional incidence ( $\alpha = 0^\circ$ )  
219 show the highest refractive index with  $n_{589} = 2.18$  and thus, the lowest porosity with  $\pi$  lower than  
220 21 %. As expected, index is below that of the bulk material because of the total sputtering pressure  
221 (0.18 Pa) used to deposit the films. Thermalisation effect of the sputtered particles and especially,  
222 intrinsic low energy bombardment in sputtered thin films are both influenced by the sputtering  
223 pressure. They can favour a structure with an open grain boundaries and large columns, leading to a  
224 significant void fraction in the deposited film. As a result, density of  $WO_3$  deposited film is lower  
225 than that of the bulk.

226 It is also worth of noting that refractive index and porosity are nearly constant up to an incident  
227 angle of  $50^\circ$ . Index rapidly drops from  $n_{589} = 2.14$  down to 1.78 when  $\alpha$  changes from  $50$  to  $80^\circ$   
228 whereas the porous structure is enhanced and  $\pi$  reaches 45 % for  $\alpha = 80^\circ$ . It is mainly attributed to  
229 the shadowing effect, which prevails on the surface diffusion of adatoms increasing the deposition  
230 angle. These results well agree with previous investigations focused on oxide thin films [47, 48].  
231 Varying the amount of bulk material in the film provides a means of tuning its optical properties  
232 according to a monotonic and continuous relationship between  $n$  and  $\alpha$ . For highly oblique angles  
233 ( $\alpha > 80^\circ$ ), refractive index should approach unity and porosity should tend to 100 %. However, the  
234 lowest index and thus the maximum porosity for  $WO_3$  coatings prepared in this study, obviously  
235 depend on the film preparation conditions, but the measurements techniques (spectrometry in  
236 transmission by Swanepoel's method, ellipsometry) and environment (humidity) can also influence  
237 the reachable index and porosity values.

238 Because of the peculiar architecture of the GLAD thin films, anisotropic behaviours like  
239 birefringence can also be expected. Thus, transmittance spectra were measured with two  $x$  and  $y$   
240 orthogonal directions of incident linear polarized light ( $T_x$  and  $T_y$  in the  $x$  and  $y$  directions,  
241 respectively and according to axes defined in Fig. 1). The in-plane birefringence is defined as the  
242 difference between the two in-plane refractive indices  $\Delta n = n_x - n_y$ , where  $n_x$  and  $n_y$  are determined  
243 by the Swanepoel's method from  $T_x$  and  $T_y$ , respectively. Figure 7 illustrates the influence of the  
244 incident angle  $\alpha$  on the birefringence  $\Delta n$  calculated at 617 nm. This birefringence first increases  
245 with the incident angle then reaches a maximum value of  $\Delta n = 0.023$  for  $\alpha = 50^\circ$ . The fact that there  
246 is an optimised birefringence was also reported by other authors for  $ZrO_2$  [42],  $ZnS$  [48],  $Ta_2O_5$  [51]  
247 or  $TiO_2$  [52] films. Furthermore, the value of the maximum  $\Delta n$  can be enhanced using a serial  
248 bideposition technique as described by Hodginkson and Wu [51]. For tilted columnar films  
249 prepared from standard oblique deposition, the highly porous structure obtained for the highest  
250 incident angles does not improve the optical anisotropy. The optimized birefringence can not solely  
251 be connected to the porosity, but rather to the biaxial columnar structure. This latter is especially  
252 produced for incident angles close to  $60^\circ$ . From simulations and experiments performed by Tait et  
253 al. [35], films produce a columnar structure with columns exhibiting an elliptical section versus the  
254 incident angle. A structural anisotropy develops parallel to the substrate surface because of the  
255 shadowing effect. This effect, mainly in the direction of the incident vapour flux, leads to the  
256 formation of growth islands connected to each other by chains perpendicular to the plane of  
257 incidence or to the direction of shadowing. The authors established that for an incident angle close  
258 to  $60^\circ$ , the shadowing effect prevails on the surface diffusion. By further increasing the  $\alpha$  angle, the  
259 number of islands falls because of shadowing effect is even more marked. Consequently, the  
260 average distance between islands increases. Then, they become disconnected from each other in all  
261 directions, resulting in a loss of anisotropy.

262 The Swanepoel's method can also be used to calculate the evolution of the absorption coefficient  $\xi$   
263 as a function of wavelength. Therefore, the optical band gap  $E_g$  of  $\text{WO}_3$  films can be determined  
264 from the Tauc's relationship according to the following equation [53]:

$$265 \quad \xi h\nu = C(h\nu - E_g)^w \quad (2)$$

266 Where  $C$  is a constant and  $w$  is 1/2, 3/2, 2 or 3 for transitions being direct and allowed, direct and  
267 forbidden, indirect and allowed, and indirect and forbidden, respectively. The values of optical band  
268 gap energy  $E_g$  can be obtained by extrapolating the absorption coefficient to zero absorption in the  
269  $(\xi h\nu)^{1/w}$  against photon energy  $h\nu$  plot. According to Hjelm et al. [54],  $\text{WO}_3$  compound exhibits  
270 indirect and allowed band gap transitions with  $w = 2$ . Thus, the  $E_g$  value was extracted from  $(\xi h\nu)^{1/2}$   
271 versus  $h\nu$  plot for  $\text{WO}_3$  films prepared with different incident angles (Fig. 8). Without inclining the  
272 particle flux ( $\alpha = 0^\circ$ ), the optical band gap  $E_g$  is 3.11 eV. It is higher than that of the  $\text{WO}_3$  bulk  
273 material, which is 2.62 eV [55] but in agreement with typical values (more than 3 eV) reported for  
274 tungsten trioxide thin films [56]. This high energy gap of oxide thin films compared to the bulk  
275 value is mainly associated to the small crystallite size (smaller than 15 nm from XRD results in Fig.  
276 2). An increase of the incident angle up to  $\alpha = 60^\circ$  does not significantly modify the optical band  
277 gap since  $E_g$  slightly decreases down to 3.05 eV. A further increase of the incident angle until  $\alpha =$   
278  $80^\circ$  leads to reduce  $E_g$  down to 2.90 eV. It can not be ascribed to the improvement of the long range  
279 order since it was shown from XRD analyses that the crystallite size reaches 30 nm for  $\alpha = 40^\circ$  and  
280 did not evolve as the incident angle  $\alpha$  increased up to  $80^\circ$  (cf. § 3.1). It is rather correlated with an  
281 increase of growth and structural defects, which are favoured for high incident angles. Thus, this  
282 decrease of the optical band gap for incident angles higher than  $60^\circ$  could be interpreted as being  
283 due to more defects in the film, creating more impurity states in the band gap.

284 It is also worth of noting that these structural defects and the short range order both facilitate the  
285 creation of disorder in the material, favouring a tail of density of states. At lower values of the  
286 absorption coefficient  $\xi$ , the extent of the exponential tail of the absorption edge is characterized by

287 the Urbach energy  $E_u$  indicating the width of the band tails of the localized states within the optical  
288 band gap. It is given by [57]:

$$289 \quad \xi h \nu = \xi_0 \exp\left(\frac{h \nu}{E_u}\right) \quad (3)$$

290 Where  $\xi_0$  is a constant. It is obvious that the plot of  $\ln(\xi)$  versus  $h\nu$  should follow a linear behaviour  
291 and allows determining the Urbach energy. This latter was systematically calculated and compared  
292 to the optical band gap  $E_g$  as a function of the incident angle  $\alpha$  (Fig. 9). An increase of the Urbach  
293 energy from  $E_u = 74$  up to 141 meV corresponds to the decrease in the optical band gap from  $E_g =$   
294 3.11 down to 2.90 eV as  $\alpha$  rises from 0 to 80°. A linear evolution of  $E_g$  versus  $E_u$  can be suggested,  
295 which is in agreement with past investigations devoted to thin films [58]. It correlates with an  
296 improvement of the crystallinity of the films observed from XRD results and corroborates similar  
297 linear evolutions previously obtained by others [59] for films going from the amorphous to the  
298 polycrystalline structure. A quantitative relationship between the values of  $E_g$  and  $E_u$  under changes  
299 in structural site disorder can be determined with linear coefficients closely linked to structural  
300 defects in the materials (bond length, bond angle, chemical disorder) [60]. For our  $\text{WO}_3$  GLAD thin  
301 films, the increase of the local disorder as the incident angle rises (increase of  $E_u$  and reverse  
302 evolution of  $E_g$ ) can be assigned to the secondary grain growth of the voided columnar structure,  
303 especially produced for very high incident angles due to a broad incident flux distribution [61]. As a  
304 result, the density of defects in the porous structure (e.g. dangling bonds) rises versus the incident  
305 angle, leading to higher Urbach energies.

306

#### 307 **4. Conclusion**

308 Tungsten oxide WO<sub>3</sub> thin films with inclined columnar structures were prepared by dc reactive  
309 magnetron sputtering. The glancing angle deposition technique was implemented to deposit these  
310 oriented columnar architectures. Then, a systematic change of the incident angle of the particle flux  
311 was performed from  $\alpha = 0$  to  $80^\circ$ . A clear columnar inclination was produced for incident angles  
312 higher than  $50^\circ$ . The resulting columnar angles were tuned from  $\beta = 0$  to  $54^\circ$  leading to an  
313 emphasized porous microstructure (45 % of porosity) for the most inclined columns. XRD analyses  
314 revealed diffracted signals corresponding to the WO<sub>3</sub> monoclinic structure with an improved  
315 crystallinity as the incident angle increased. Similarly, optical properties like refractive index and  
316 extinction coefficient were calculated from optical transmittance measurements in the visible  
317 region. Refractive index was significantly reduced from  $n_{589} = 2.11$  down to 1.90 as the incident  
318 angle increased from  $\alpha = 0$  to  $80^\circ$ . Extinction coefficient remained nearly constant and close to  $k_{589}$   
319  $= 1.50 \times 10^{-3}$  up to  $\alpha = 60^\circ$  then became higher than  $4.27 \times 10^{-3}$  for the highest incident angles.  
320 Variations of the optical behaviours were correlated to the highly porous structure. Voids separating  
321 the oriented columns become more significant for incident angles higher than  $\alpha = 60^\circ$  because of  
322 the shadowing effect prevailing over the surface adatoms diffusion. Voids and pinholes observed  
323 are asymmetric in the x- and y-directions, which introduce anisotropy and birefringence in thin  
324 films. The maximum in-plane birefringence was found to be  $\Delta n = 0.023$  for an incident angle of  
325  $50^\circ$ . A linear and reverse evolution of the optical band gap versus Urbach energy was noticed with a  
326 systematic change of the incident angle, which was correlated with an increase of the density of  
327 defects in the highest porous structures.

328

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415 **Figure captions**

416 Figure 1

417 Surface and cross-section observations by SEM of WO<sub>3</sub> thin films sputter deposited on (100) Si  
418 with two different incident angles  $\alpha$  of the sputtered particles: a) and b)  $\alpha = 70^\circ$ ; c) and d)  $\alpha = 80^\circ$ .  
419 Direction of incoming particle flux, incident angle  $\alpha$ , column angle  $\beta$  and  $(x, y, z)$  axes are  
420 indicated. The scale bar is the same for all images.

421

422 Figure 2

423 X-ray diffraction patterns of the tungsten oxide thin films deposited on (100) Si with various  
424 incident angles  $\alpha$  of the particle flux ( $\alpha = 0, 40$  and  $80^\circ$ ). Diffracted signals (\*) corresponding to the  
425 monoclinic WO<sub>3</sub> structure are detected (Si = silicon substrate).

426

427 Figure 3

428 Optical transmittance spectra in the visible range of tungsten oxide thin films deposited on glass  
429 substrate for incident angles  $\alpha = 0, 40$  and  $80^\circ$ . Clear interference fringes are measured, which are  
430 typical of transparent thin films.

431

432 Figure 4

433 Refractive index  $n$  as a function of wavelength  $\lambda$  in the visible range for tungsten oxide thin films  
434 deposited on glass substrate with incident angles  $\alpha = 0, 40, 60$  and  $80^\circ$ . A Cauchy dispersion law  
435 was used to fit the evolution of  $n$  versus  $\lambda$ .

436

437 Figure 5

438 Extinction coefficient  $k$  as a function of wavelength  $\lambda$  in the visible range for tungsten oxide thin  
439 films deposited on glass substrate with incident angles  $\alpha = 0, 40, 60$  and  $80^\circ$ .

440

441 Figure 6

442 Refractive index  $n_{589}$  at  $\lambda = 589$  nm and porosity  $\pi$  of  $\text{WO}_3$  thin films versus incident angle  $\alpha$ .  
443 Porosity was determined from the packing density based on the Bruggemann effective medium  
444 approximation. Incident angles higher than  $50^\circ$  lead to the most significant changes of the refractive  
445 index and porosity. Dashed lines are guides for the eye.

446

447 Figure 7

448 In-plane birefringence  $\Delta n$  at  $\lambda = 617$  nm for  $\text{WO}_3$  thin films as a function of the incident angle  $\alpha$ . A  
449 maximum of anisotropy is obtained for an incident angle of  $50^\circ$ . Dashed line is guide for the eye.

450

451 Figure 8

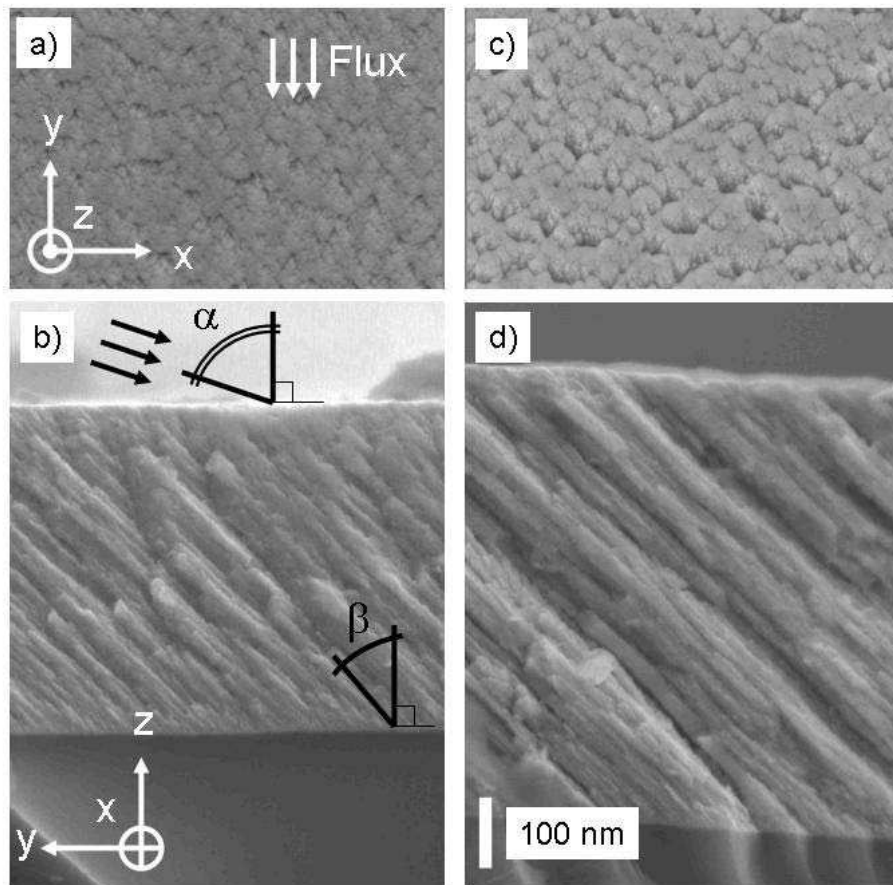
452 Typical plot of the absorption coefficient  $(\alpha h\nu)^{1/2}$  versus photon energy  $h\nu$  for  $\text{WO}_3$  thin films  
453 prepared for incident angles  $\alpha = 0, 40$  and  $80^\circ$ . Indirect and allowed transitions were assumed to  
454 deduce the optical band gap according to the Tauc's relationship. Solid lines in the figure refer to  
455 extrapolation for determining the optical band gap.

456

457 Figure 9

458 Linear evolution of the optical band gap  $E_g$  as a function of Urbach energy  $E_u$  of  $\text{WO}_3$  thin films  
459 deposited with a systematic increase of the incident angle  $\alpha$  from  $0$  to  $80^\circ$ . Dashed line is guide for  
460 the eye.

Figure 1



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Figure 2

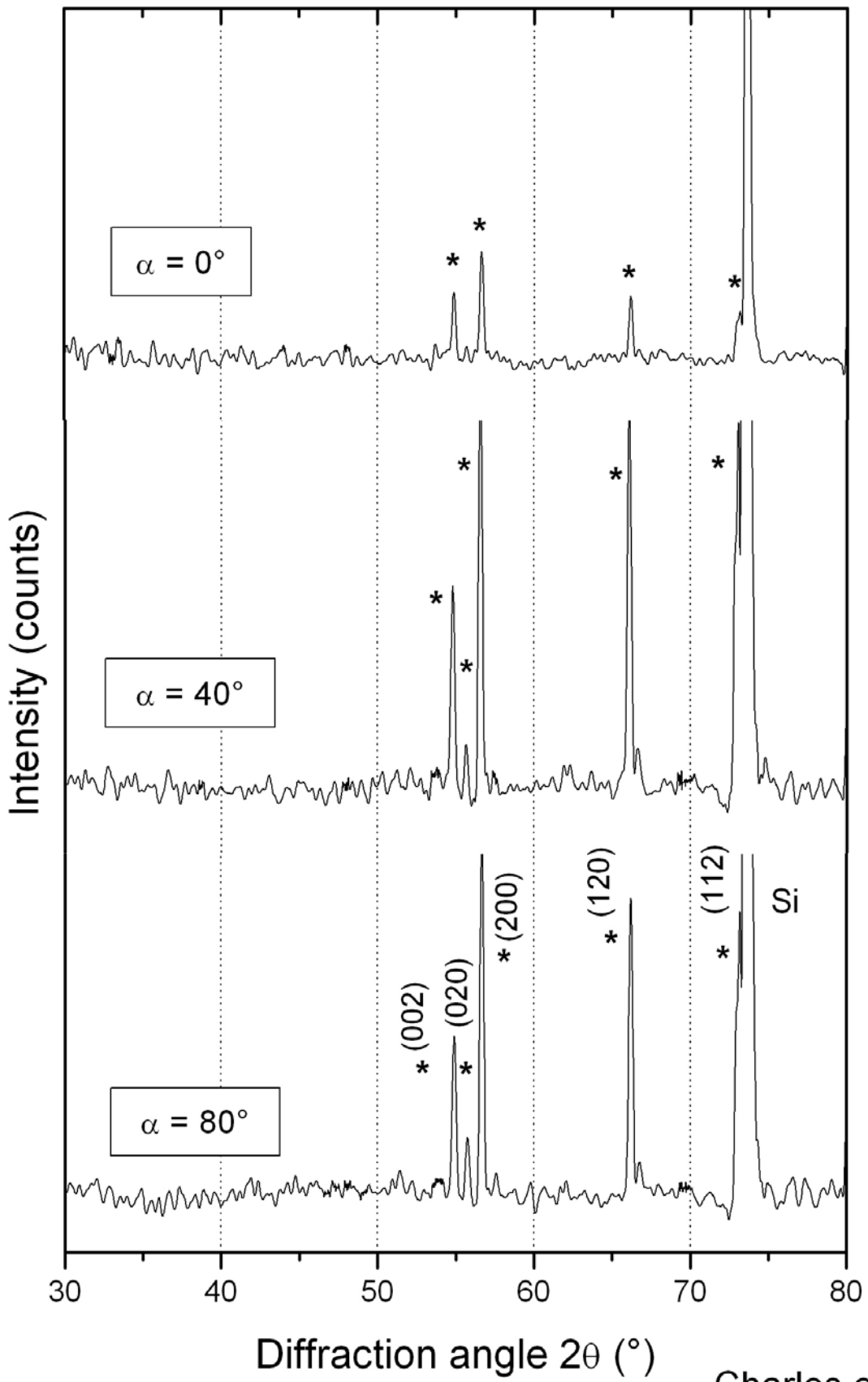


Figure 3

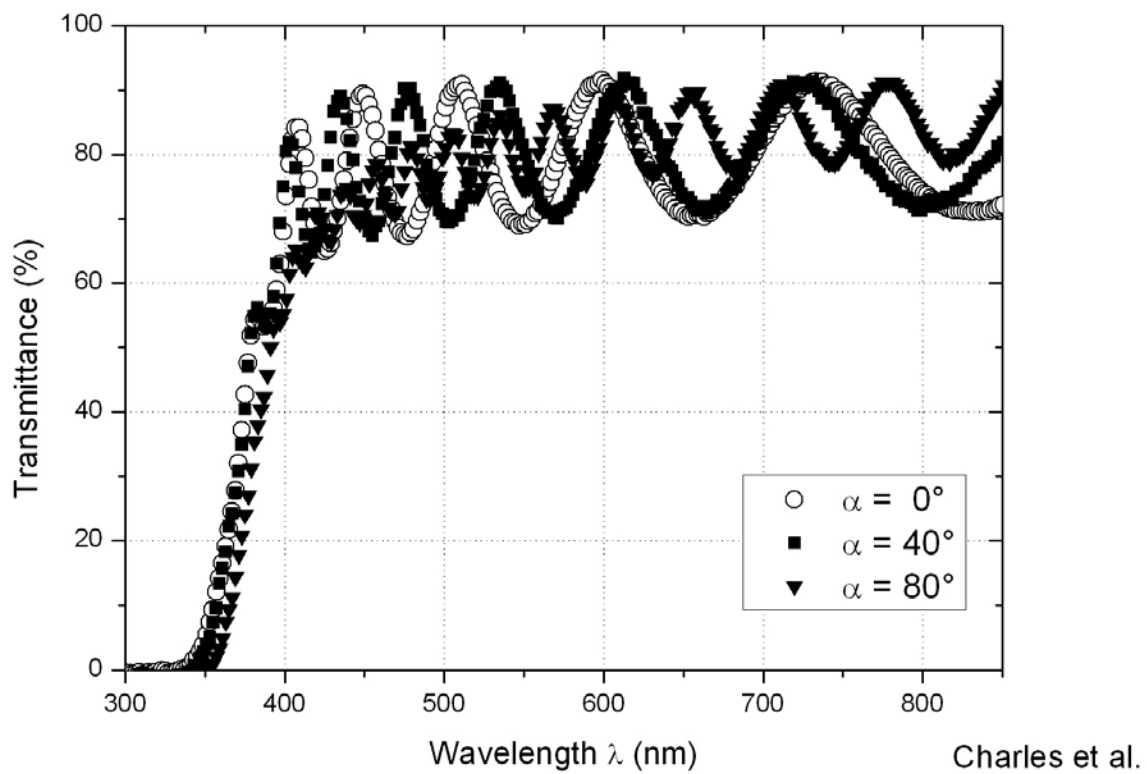
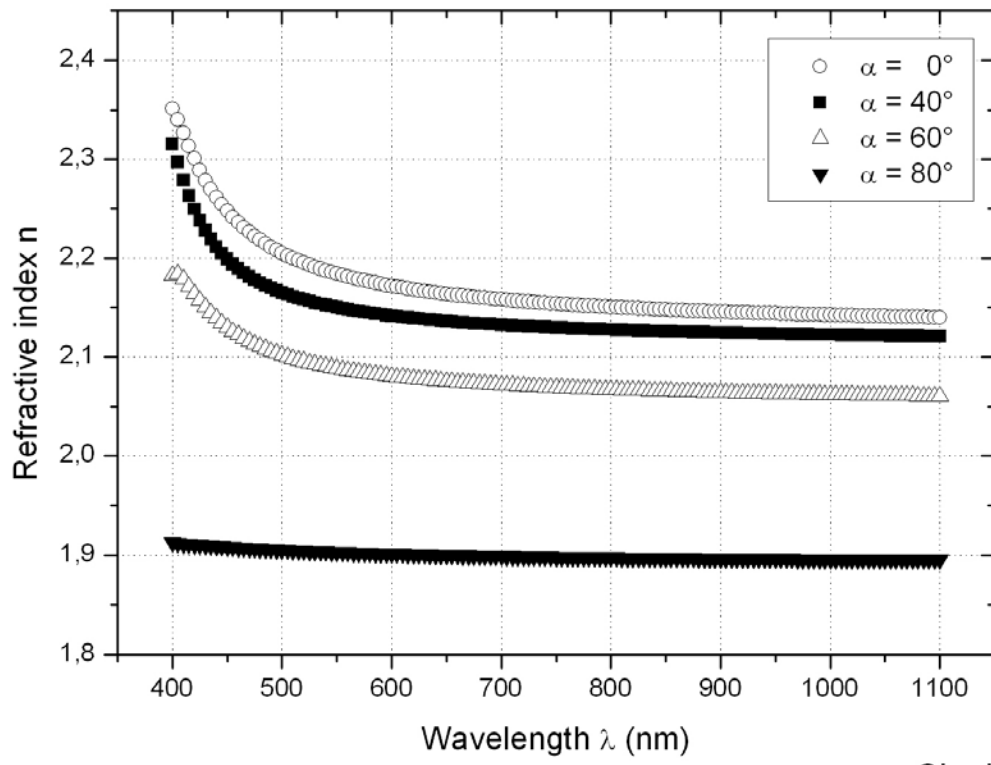




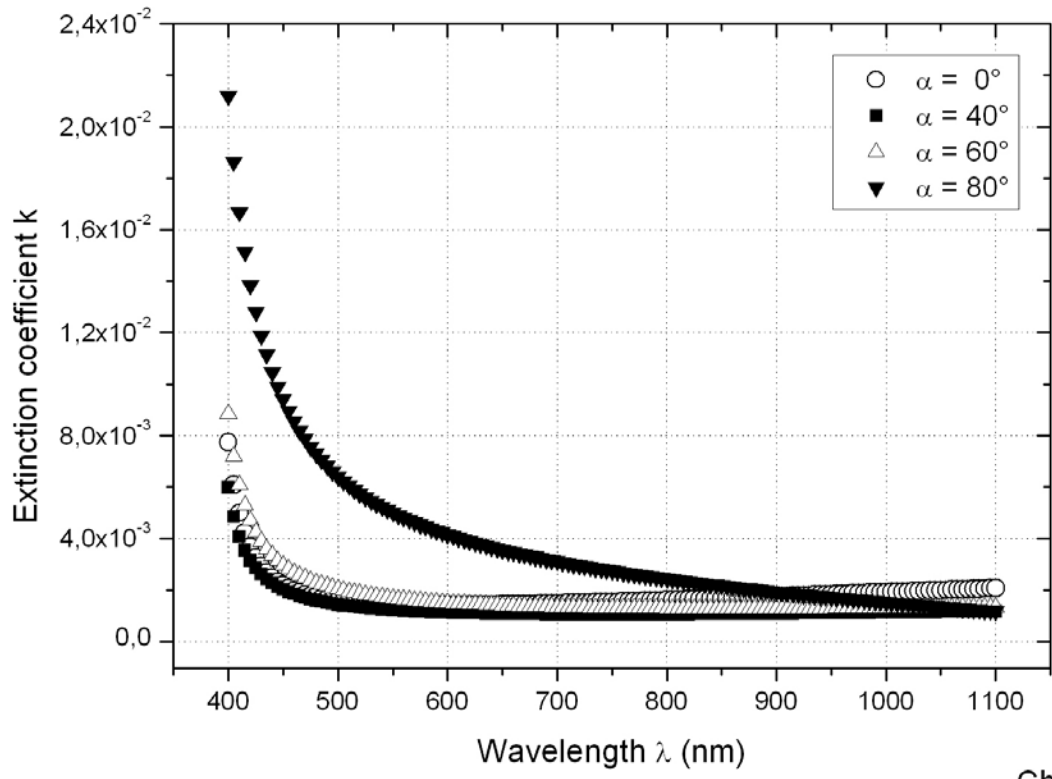
Figure 4



464

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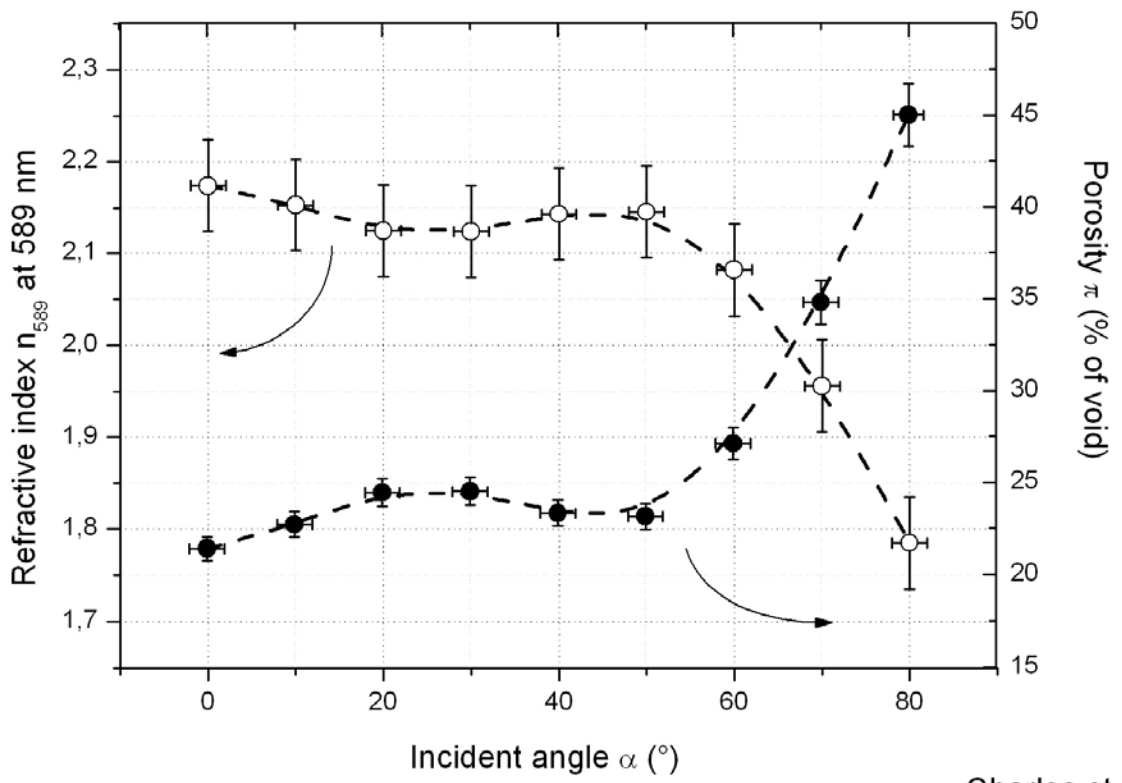
Figure 5



465

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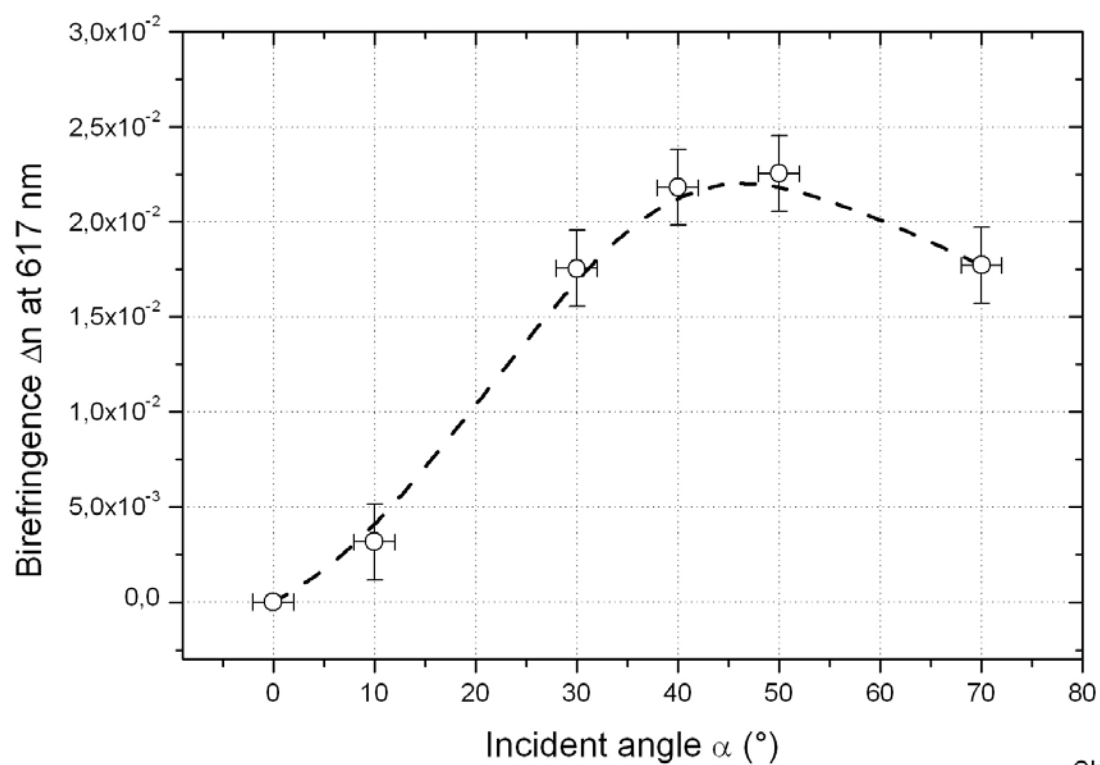
Figure 6



466

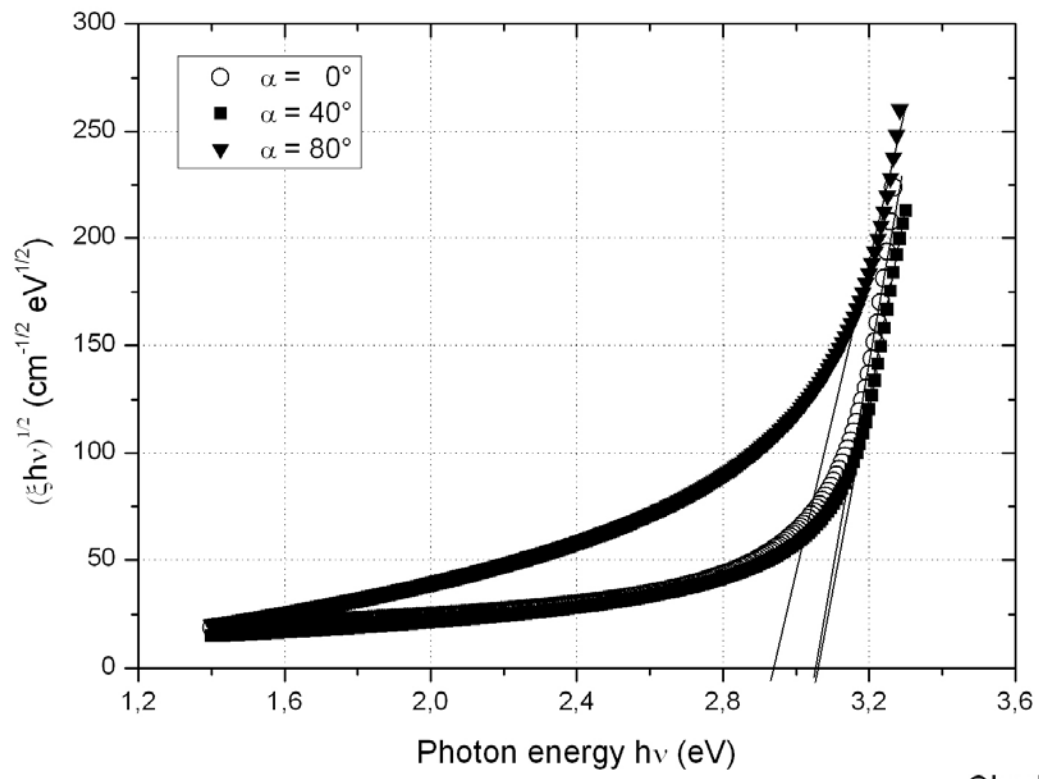
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Figure 7



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Figure 8



468

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Figure 9

