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**Physical properties investigation of ion assisted-ZrN thin films
deposited by RF magnetron sputtering**

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Abstract

Ion bombardment during thin film growth is known to cause structural and morphological changes in the deposited films and thus affecting their physical properties. In this work zirconium nitride films have been deposited by ion assisted magnetron sputtering technique. The ion energy is controlled by varying the voltage applied to the substrate in the range 0 – 25 V. The deposited ZrN films are characterized for their structure, surface roughness, oxygen contamination, optical reflectance and electrical resistivity. With increasing substrate voltage films cristallinity is enhanced with a preferential orientation of the ZrN grains having the (111) axis perpendicular to the substrate surface. In the same time, a decreasing in the electrical resistivity and in the oxygen contamination content is observed up to 20 V. A higher substrate voltage (25 V) causes an inversion in the observed experimental trends. The role of oxygen contamination decrease and nitrogen vacancies generation due to the ionic assistance has been considered as possible explanation of the experimental results.

Introduction

The properties of thin films grown by physical vapor deposition (PVD) processes strongly depend on the incident particles energy transferred to surface of growing films [1]. This energy available on the films surface can promote many phenomena such as the enhancement of surface atom mobility [2], modification of the cristallinity [3], variation in the composition [4], structure and

microstructure and, as consequence, in the physical response of the deposited material. Ion bombardment permits to obtain denser and void-free films [5] even by performing a low temperature deposition process which sometimes is more convenient and advantageous [6]. The simplest way to achieve ion bombardment on the growing film during plasma growth process is biasing the substrate during the deposition. The bias voltage applied to the substrate attracts ions (argon and nitrogen) out from the plasma towards the substrate by the potential drop in the sheath region. At a fixed process total pressure, the energy of these ions [7] will be proportional to this voltage. For small bias voltages, the sheath at the substrate will be thin enough that it will be collision free [8]. In the present investigation RF reactive magnetron sputtering process was used to grow thin films of ZrN, a material which is remarkably stimulating the scientific interest for its wide field of applications [9]. During the deposition process the reactive gas mixture total pressure, the substrate temperature and the power applied to Zr target were kept constant, while a negative bias voltage was applied to the substrate in the range 0 – 25 V. A (111) texture has been obtained for ZrN films and a low electrical resistivity ($\sim 160 \mu\Omega \cdot \text{cm}$) has been achieved for the 20 V-biased sample. The role of oxygen and of nitrogen vacancies has been qualitatively discussed for the experimental results interpretation. Therefore, in this work it is shown how the optimization of substrate bias can simultaneously improve ZrN films electrical conductivity and texture. The improvement of these two properties makes ZrN a good candidate as diffusion barrier in microelectronics device where low resistivity and high texturing are requested besides good adhesion, chemical inertness with copper and silicon and high thermal stability [10]. An excellent diffusion barrier behavior has been found for ZrN (111)-oriented [11] but this orientation has been gained at high deposition temperature, while in this work the application of a substrate bias leads to high texturing at room temperature.

53 1. Experimental details

54 ZrN films were deposited on silicon wafers (100)-oriented by reactive RF magnetron sputtering in
55 an Ar/N₂ gas mixture. Both gases were 99.999 % pure. The working pressure was kept constant at a
56 value of $1.12 \cdot 10^{-2}$ Torr and the nitrogen flux percentage in the mixture was fixed at 5 %. The power
57 applied to Zr target during the deposition was 165 W. The distance between the substrates and the
58 target was 70 mm. The substrate temperature was monitored by a thermocouple and it did not
59 overcome 70 °C during the whole process. The only tuned process parameter was the negative bias
60 voltage applied to the substrate in the range 0 – -25 V with respect to the ground. As simplification,
61 in the text the voltage absolute values will be indicated. Before the nitride films deposition, the
62 target was pre-sputtered in argon atmosphere for about half an hour. The films are about 500 nm-
63 thick. The thickness was measured using a profilometer (KLA TENCOR) on steps patterned by a
64 solid mask. The morphology and the roughness of films were investigated by atomic force
65 microscopy (AFM). The AFM measurements were performed with a Nanoscope III from Digital
66 Instruments. Silicon cantilevers with radius less than 10 nm was used as tip. All measurements were
67 performed in tapping mode in air. The X-ray diffraction and reflectivity experiments were carried
68 out by using an X-ray diffractometer in parallel beam geometry (Philips MPD PW1880, 3 kW
69 generator) optimized for small-angle scattering measurements. For all the measurements Cu_{Kα}-
70 radiation ($\lambda_{\text{CuK}\alpha}=0.154186$ nm) was used. The X-ray diffraction measurements were performed
71 under different geometrical configurations, i.e. by performing both θ -2 θ scan as well as grazing
72 incidence (with fixed incidence angle $\omega_i=1.0^\circ$) measurements. The grazing-incidence measurements
73 (GIXRD) were performed by keeping the incident angle ω_i (angle between incident beam and
74 sample surface) fixed at 1.0° and recording the scattered X-ray beam by moving the detector and
75 post-sample flat graphite collimator-monochromator along the goniometer circle in the 2 θ range
76 between 10° and 100° with a step size of 0.02° . The θ -2 θ scan were measured in the angular 2 θ
77 range between 25° and 45° with a step size of 0.01° , because the Bragg peaks in only these angular

range were intense enough to be analyzed quantitatively. Within the X-ray reflectivity (XRR) regime, we have taken specular ($\omega, 2\theta$) scans (XSR) in which the grazing angle of incidence of the X-rays is equal to the exit angle (measured 2θ range between 0° and 9° with a step size of 0.01°), and transverse ω scans (XDS, diffuse scattering) in which the angular position of slit and detector (2θ angle) was fixed. DC electrical resistivity at room temperature was deduced from sheet resistance measurements using the four point-probe method. A CARY 500 spectrometer was employed to perform optical reflectance measurements in the range from 200 to 2500 nm. Standard SIMS measurements have been performed by means of a CAMECA ims4f magnetic sector instrument by using Cs^+ primary ions and detecting Zr^+ and MCs^+ ($\text{M} = \text{O}, \text{N}$) secondary ions [12].

87

2. Results

2.1 Structure and morphology of the films

Generally, for thin films with layer thickness $< 1 \mu\text{m}$ and nanocrystalline structure grazing incidence diffraction measurements (GIXRD) are more appropriate for a quantitative analysis since the X-ray penetration depth is reduced and the relative Bragg peak intensity is enhanced. The grazing-incidence diffraction (GIXRD) and X-ray reflection (XSR) schemes are schematically shown in Fig.1. Both measurements are carried out in co-planar scattering geometry. However, in the GIXRD configuration (Fig.1a) the incidence angle ω_i between incident X-ray beam ($\mathbf{k}_0$) and sample surface is kept constant, while the intensity of the diffracted X-ray beam ($\mathbf{k}_h$) is recorded for different 2θ angles. On the contrary, for the X-ray specular reflectivity measurements (Fig.1b) the scattered X-ray intensity is recorded keeping the angles between the sample surface and the incident and reflected X-ray beams, respectively, equal. In this case (b), the scattering vector $\mathbf{h}$ is parallel to the surface normal $\mathbf{n}$. Figure 2 shows the GIXRD patterns of the samples deposited with a negative V_{bias} of 0 V, 10 V and 25 V, respectively, in the 2θ angular range between 10° - 100° . Several Bragg peaks are well observed and can be identified in accordance with the PDF 74-1217 [13] of the

103 cubic phase of ZrN. The θ - 2θ measurement patterns are shown in Figure 3. The 2θ as well the θ - 2θ
 104 measurements show very clearly that the relative intensity of the (111) Bragg peaks increases while
 105 the width (FWHM) of the (111) and (200) Bragg peaks reduces with the increasing negative bias
 106 voltage V_{bias} applied during sputtering deposition. The average ZrN particle size was estimated
 107 from the broadening of the (111) and (200) diffraction peaks by using a Cauchy fit of the peak
 108 profiles and applying the Scherrer's formula [14]:

$$109 \quad D = 0.94\lambda / (\Delta\omega \cos \theta_B) \quad (1)$$

110 where D is the average crystallite size, λ is the X-ray wavelength, $\Delta\omega$ is the calculated FWHM of
 111 the diffraction peak in radians and θ_B is the Bragg angle. The grain size increases linearly with
 112 increasing bias voltage V_{bias} starting from 5.1 nm to 14.5 nm, for $V_{\text{bias}}=0$ V and 25 V, respectively.
 113 The results are depicted in Figure 4 and summarized in Table 1. In addition, the diffraction patterns
 114 in Figures 2 and 3 show that the relative intensity ratio between the Bragg peaks does not
 115 correspond to the expected values as reported in the PDF 74-1217; for example the (200) Bragg
 116 peak intensity should be only slightly lower than the (111) Bragg peak intensity by about 15 % .
 117 Furthermore, the relative (111) peak intensity increases with increasing applied bias voltage V_{bias} .
 118 These findings indicate a pronounced extension of the ZrN grains along the (111) crystallographic
 119 axis and a preferential orientation of the ZrN grains having the (111) axis perpendicular to the
 120 substrate surface, i.e. parallel to the deposition/growth direction. This texture of the closest packed
 121 plane is the most frequently encountered in fcc structure such as zirconium nitride [15, 16]. A
 122 pronounced angular deviation of all the most intense Bragg peaks of the GIXRD as well as the
 123 XRD patterns is observed. In particular the angular shift of the (111) Bragg peak in Figure 3 is
 124 clearly visible. A reliable and accurate determination of the angular peak positions (by employing a
 125 peak profile fitting) is only possible for the most intense Bragg peaks, i.e. the (111), (200), (220)
 126 and (311) peaks. The increase of the angular position of the diffraction peaks with the bias voltage
 127 corresponds to the decrease of the lattice constant, whose values have been determined from the
 128 Bragg's law and reported in Figure 5 and in Table 1. It should be noted that the value reported for c-

ZrN is about 4.63Å [12]. Specular X-ray reflectivity (XSR) and transverse scan (XDS) measurements were performed in order to investigate the surface morphology, the density and the chemical compositional of the deposited ZrN films. Figure 6 shows the XSR and the transverse scans recorded for different 2θ positions of the samples assisted at $V_{\text{bias}} = 0$ V and $V_{\text{bias}} = 10$ V. The XSR patterns shows a very fast decay of the reflected intensity above the critical angle. The fast intensity decay observed above the critical angle θ_c indicates a high surface roughness (≥ 5 nm), however, its precise value can not be determined within the Nevot-Croce model that yields typically reliable data for RMS roughness < 5 nm. The determination of the critical angle values (reported in Table 1) through the angular position of the fast intensity decay of the XSR pattern and of the Yoneda peaks positions allows us to determine the mass density (or the real part of the dielectric susceptibility) of the deposited ZrN films. The mass density is related to the critical angle θ_c by the equation [13]:

$$\rho_m = \frac{\pi \cdot \theta_c^2}{r_e \cdot \lambda^2 \cdot N_A} \cdot \frac{\sum_i (Z_i + f_i')}{\sum_i M_i} \quad (2)$$

where r_e is the classical electron radius, λ is the X-ray wavelength used, N_A is the Avogadro's number, and Z_i , f_i' and M_i are the nuclear charges, the dispersion corrections and the atomic weights of the i -th chemical element, respectively. The mass density of the deposited ZrN films as a function of the applied bias voltage V_{bias} has been evaluated by using Eq. (2) and is shown in Figure 7 where it is clear that its increasing follows the voltage rise.

147

	negative bias voltage V_{bias} (V)	grain size D (nm) (± 0.5)	lattice parameter c (Å) (± 0.0013)	critical angle θ_c (deg) (± 0.007)	Mass density (g/cm³)	RMS roughness (nm)
	0	5.1	4.6768	0.30	4.82	5.5
	10	8.3	4.6232	0.32	5.48	6.7
	20	10.2	4.5855	0.335	6.00	10.8
	25	14.5	4.5921	0.35	6.56	10.8
c- ZrN	-	-	4.63	0.364	7.09	-

148

Table 1 – Physical parameters (lattice parameter, grain size, critical angle, mass density) as determined from XRD and XRR measurements and RMS roughness values evaluated by AFM measurements.

AFM micrographs (Figure 8) give evidence of all the deposited samples topography. They exhibit a “cauliflower-like” surface which can be observed when a thin film has a columnar structure with grain size of tens of nanometers [17], as previously confirmed by XRD analysis (Fig. 4). The evaluated average root mean-square roughness (RMS) is in the range of 5-11 nm as reported in the last column of Table 1 corroborating XSR results which evaluate a surface roughness values higher than 5 nm.

2.2 Optical and electrical analyses

The characteristic feature of the reflectance spectra is a distinct minimum located in the range between 2.8 eV and 3.5 eV, followed by a sudden rise, the so called “plasma reflectance edge” [18], at lower energies (Fig. 9). The high reflectance in the IR range is related to the high light absorption by the free electron gas (conduction electrons, described by the Drude model), while the reflectance in the UV range is related to the absorption by the interband transitions of the bounded electrons (described by the Lorentz oscillators). As a consequence, the reflectance spectra can be fitted by the use of a model including a Drude part and one or more Lorentz oscillators. The energy of the reflectance minimum, the reflectance percentage at 0.8 eV and the plasma energy of the Drude part are listed in Table 2. A detailed analysis of the optical spectra by a Drude-Lorentz model is in progress and it will be reported in a future paper.

The energy of the reflectance minimum shifts to higher energy when the voltage increases up to 20 V, then it slightly decreases for the film assisted at 25 V. At the same time, the reflectance in the low energy range also increases with the applied bias voltage until 20 V, and it slightly decreases at 25 V. Both these behaviors are reported in the inset of Fig. 9. The plasma energy value follows the same trend, as it has an increase until 20 V and a following decrease at 25 V (see Table 2).

$-V_{\text{bias}}$ (V)	Energy of the reflectance minimum (eV)	Reflectance percentage at 0.8 eV (%)	Plasma energy (eV)	Resistivity ($\mu\Omega \cdot \text{cm}$)
0	2.8	24.6	1.8	13240
5	3.0	32.3	2.7	4020
10	3.1	36.4	3.2	2300
15	3.3	52.6	4.9	336
20	3.5	68.8	6.9	159
25	3.3	47.6	4.0	280

Table 2 – Values of the energy of the reflectance minimum, the reflectance percentage at 0.8 eV, the plasma energy and the electrical resistivity as determined by optical and electrical analyses.

A similar behavior can be observed in the electrical measurements too. Indeed the general result obtained by four-point probe method measurements is that the application of a bias voltage greatly lowers the electrical resistivity down to a minimum value at 20 V, after which an inversion is observed, as reported in Figure 10 and in Table 2. In particular, the unbiased ZrN film exhibits the highest resistivity value (13240 $\mu\Omega\cdot\text{cm}$) that is lower than the value found by Pilloud et al. [15] (27000 $\mu\Omega\cdot\text{cm}$) evaluated by the same technique. The lowest resistivity value in our samples is $\sim 160 \mu\Omega\cdot\text{cm}$, which is comparable with the lowest value found in ref. [15] ($\sim 150 \mu\Omega\cdot\text{cm}$). However it is noteworthy that in our case this low value is obtained at a bias voltage value of 20 V, far lower than that used in [15] (160 V). In the analyzed negative bias voltage range (0 – 25 V) the electrical resistivity of the ZrN films is at least one order of magnitude higher than that of the bulk material (13.6 $\mu\Omega\cdot\text{cm}$) [19], as already noted by other authors [20, 21].

2.3 Oxygen contamination: SIMS analysis

Oxygen contamination is the most challenging problem for films deposition by PVD process, above all for transition metal nitrides due to the strong affinity of the metal with oxygen. To verify the oxygen incorporation, SIMS analysis was performed on all deposited samples by monitoring the CsO^+ molecular ion. The exact composition cannot be determined by the SIMS measurement due to a lack of a standard reference ZrN material. Therefore, the ratio of the oxygen signal number to the

total signal number of the films elements (Zr, O and N) was calculated as qualitative indication. In particular these values have been normalized respect to the 20 V-assisted oxygen signal taken as reference and reported in Figure 11. Although these values do not correspond to the exact chemical composition, it is possible to compare the relative oxygen content in the different samples. They indicate that the oxygen amount is approximately the same in the first three samples (0, 5, 10 V), while it decreases biasing the substrate at 15 and 20 V, then it slightly increases again for the sample deposited at 25 V.

3. Discussion

The main remarkable effects related to the increasing of the substrate bias voltage observed in our study are: a pronounced preferential orientation of the ZrN grains along the (111) crystallographic axis, a rising of films density and grain size, a decreasing of lattice parameter and electrical resistivity, a shift of the reflectance minimum towards higher energy and an increasing of the reflectivity percentage in the near infrared region.

The (111) preferential orientation results from the increasing kinetic energy and momentum of incident ions with the increasing bias voltage at a constant deposition pressure [22], inducing intrinsic compressive stresses in the films through atoms substitution or vacancies generation [23]. In this case, the strain energy determines the overall energy of the films, and (111) would become the preferred orientation to minimize it [24]. It is noteworthy that the bias voltage in our films does not have any significant effect on film adhesion, while higher bias voltages (> 25 V) led to some film detachment from the substrate, probably due to the higher intrinsic compressive stress induced in the film.

The observed experimental results can be similarly attributed to two different causes: nitrogen replacement by oxygen or nitrogen vacancies generation in the ZrN lattice. Indeed, considering the lattice parameter, its decreasing down to values lower than the bulk one ($4.63 \text{ \AA}$) by rising the assistance energy, can be ascribed to stress introduced in the lattice due to nitrogen vacancies [25]

231 or to nitrogen substitution by oxygen atoms [26]. In the first case the presence of nitrogen vacancies
 232 can influence the film lattice parameter without inducing strong structural alterations: it is known
 233 that transition metal nitrides have vacancy defect structure which are stable over a wide range of
 234 composition allowing a change in the stoichiometry without altering the NaCl crystal structure [27].
 235 In particular, this has been noted also for nitrogen-deficient ZrN films [28]. In the second case, O
 236 atoms presumably tend to substitute N atoms because they are too large to be inserted into the
 237 interstitial sites of ZrN lattice causing a lattice parameter decreasing [29]. For this reason, the
 238 examination of the experimental results can help to qualitatively distinguish the respective influence
 239 of both factors.

240 According to the SIMS oxygen signals, the samples can be grouped into three classes: films
 241 deposited with V_{bias} in the range 0-10 V (I) where the oxygen content is almost the same, the 15 V
 242 and 20 V-assisted samples (II) where the contamination content quickly decreases and the 25 V-
 243 assisted sample (III) where the oxygen content slightly increases again.

244 Although the oxygen quantity is the same for the samples belonging to the group I, their physical
 245 properties significantly change: the cristallinity is enhanced (the FWHM of ZrN(111) peak
 246 decreases) thanks to the adatom mobility enhancement related to the increased bombardment energy
 247 which allows the grain growth and the films mass density improvement [30]; the electrical
 248 resistivity decreases of about six times changing from $13240 \mu\Omega\cdot\text{cm}$ (0 V) to $2300 \mu\Omega\cdot\text{cm}$ (10 V);
 249 the reflectance minimum shifts of about 0.3 eV to higher energies from 0 V to 10 V, the reflectance
 250 percentage in the near infrared region and the plasma energy rise from $\sim 25 \%$ to $\sim 36 \%$ (measured
 251 at 0.8 eV) and from 1.8 eV to 3.2 eV, respectively. Since the oxygen content in these films is almost
 252 unchanged, these variations can be mainly attributed to the changes in the presence of nitrogen
 253 vacancies, probably due to a preferential re-sputtering of nitrogen atoms during the ion assistance.
 254 In particular, the non-assisted sample exhibits the highest lattice parameter, even higher than the
 255 value in the bulk material, thus suggesting the lowest nitrogen vacancies content. This is in
 256 agreement with the optical and electrical measurements. Indeed the plasma energy is proportional to

the square root of the free electron density, therefore the increase of its value and the corresponding shift of the reflectance minimum toward high energy indicate an increase of the free electron density. At the same time the reflectance in the low energy range, related to free electrons, increases when increasing the bias voltage from 0 to 10 V. These observations indicate an increase of the free electron density with the bias voltage, in accordance with the electrical resistivity measurements, showing a decrease of the resistivity. This can be explained considering that the formation of zirconium nitride implies the transfer of electrons from the d-band of zirconium atoms to the p-states of nitrogen ones according to the ionic model of the transition metal nitride [17], so a decrease of nitrogen content causes an increase of the number of free electrons supplied by Zr atoms since these electrons are not involved in the bonds with the missing N atoms. As a confirmation, in the literature a shift of the reflectance minimum to high energies has been observed when decreasing the nitrogen content in ZrN films [31].

The decrease of the oxygen content in samples of group II causes an additional increase of the free electron density, thus further inducing a shift of the reflectance minimum (up to 3.5 eV) and an increase of the reflectance intensity in the low energy range (up to ~ 69 %) and of the plasma energy (almost 7 eV), and a decrease of the electrical resistivity (down to ~ 160 $\mu\Omega\cdot\text{cm}$). The electrical conductivity is also improved by the decreasing of the electron scattering probability due to both the reduction of oxygen impurities and the increase of film mass density with the bias voltage.

The slight inversion in the trend of the optical and electrical measurements observed for the film grown with V_{bias} of 25 V (group III) can be ascribed to two factors: (i) the high energy bombardment can produce structural defects so that the electrons are captured in defect states, thus inducing a reduction of the free electron density, and consequently a shift of the reflectance minimum to low energy (3.3 eV), a decrease of the reflectance percentage in the IR range (~ 48 %) and of the plasma energy (4 eV), and an increase of the electrical resistivity (280 $\mu\Omega\cdot\text{cm}$); (ii) the increased ions bombardment leads to an implantation phenomenon which incorporates oxygen

atoms in the films (as shown by the oxygen SIMS signal) causing the same effects mentioned above.

As already mentioned, the electrical behavior is in agreement with the optical one, since the electrical resistivity follows the same trend of the plasma energy and thus of the free electron density derived from the optical reflectance spectra. Further investigations are in progress in order to better evaluate the dependence of the resistivity on the carrier relaxation time, for example due to the grain size.

Conclusions

The negative bias voltage applied to the substrate during the sputtering deposition of zirconium nitride films has significant influence on the structural, compositional, electrical and optical properties of the ZrN films. The films exhibit a highly (111) preferred orientation due to the minimization of the strain energy. The lattice parameter decreases by rising the bias and this effect can be due to the nitrogen replacement by oxygen or to nitrogen vacancies generation caused by the ion bombardment. The simultaneous examination of the different characterizations (SIMS, optical reflectance and electrical resistance) allowed to qualitatively discriminate the influence of the two effects. The trends observed in the optical reflectance and electrical resistivity measurements are in agreement with an increase of nitrogen vacancies content with increasing the bias voltage until 20 V. A minimum resistivity value of $\sim 160 \mu\Omega\cdot\text{cm}$ is obtained for the film deposited with a negative bias voltage of 20 V. The assistance by a higher bias voltage (25 V) is found to cause an inversion in the trends observed in the contamination, optical and electrical film properties.

Captions

Figure 1: Co-planar X-ray scattering geometries used for the GIXRD (a) and XSR (b) measurements, respectively. Here, $\mathbf{k}_0$ and $\mathbf{k}_h$ are the incident and scattered X-ray beams, and $\mathbf{h}$ and $\mathbf{n}$ are the scattering vector and surface normal, respectively.

Figure 2: GIXRD measurements (2θ scans) of the same samples deposited under different bias voltage V_{bias} conditions. The Bragg peaks are indexed in accordance with the PDF 74-1217 of the JCDPS-ICDD database and corresponds to the c-ZrN ($a_{\text{ZrN}}=4.63\text{\AA}$)

Figure 3: XRD measurements (θ - 2θ scans) of samples deposited under different bias voltage V_{bias} conditions. The dashed lines indicate (111) and (200) peaks position according to the PDF 74-1217 card.

Figure 4: ZrN grain size as a function of the applied bias voltage V_{bias} . An almost linear relationship is observed for the considered experimental conditions.

Figure 5: Lattice parameter as a function of the applied negative bias voltage V_{bias} . An almost linear relationship is observed for the considered experimental conditions.

Figure 6: The XSR and the transverse scans recorded for different 2θ angular positions of the samples assisted at $V_{\text{bias}} = 0\text{ V}$ (a) and at $V_{\text{bias}} = 10\text{ V}$ (b). The dashed line indicates the angular position of the critical angle (angular position of the low-angle Yoneda wing).

Figure 7: The mass density of the deposited ZrN films increases linearly with the increasing applied bias voltage V_{bias} . The theoretical value of c-ZrN the mass density is indicated by the line.

Figure 8: AFM micrographs of the samples deposited at different applied substrate bias voltage as indicated in each picture. The roughness values are calculated on $(2\times 2)\mu\text{m}^2$ areas.

337

338 **Figure 9:** Reflectance spectra of the films deposited at different applied substrate bias voltage. Inset:
339 dependence of the energy of the reflectance minimum (solid squares, left axis) and of the reflectance
340 percentage at 0.8 eV (empty circles, right axis) on the applied bias voltage.

341

342 **Figure 10:** Dependence of the electrical resistivity (Log scale) on the substrate bias voltage.

343

344 **Figure 11:** Relative oxygen content versus substrate voltage as derived by SIMS measurements. Each value
345 has been normalized respect to the signal of the 20 V-assisted sample taken as reference.

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