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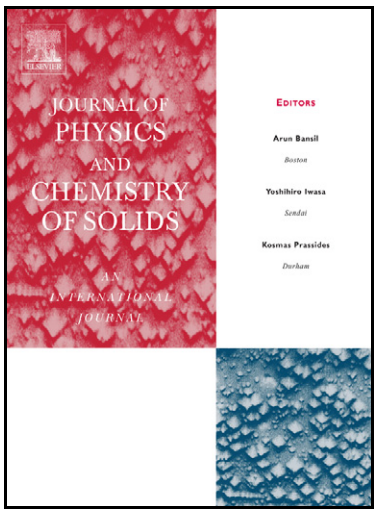

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NanocrystallineAu:Ag:SnO_2films prepared by pulsed magnetron sputtering

A. Sivasankar Reddy, N.M. Figueiredo, A. Cavaleiro*

SEG-CEMUC-Department of Mechanical Engineering, University of Coimbra, Rua Luís Reis Santos, P-3030 788 Coimbra, Portugal

Abstract

Influence of annealing temperature on structural, compositional, surface morphology, electrical, and optical properties of pulsed magnetron sputtered nanocrystalline Au:Ag:SnO_2 films were investigated by several analytical techniques. From the XRD results, the films were polycrystalline with absence of impurity phases and the films were grown preferentially in the (110) orientation of SnO_2 with tetragonal structure. The surface smoothness and grain size of the films increases with annealing temperature. Photoluminescence measurements show that the as deposited Au:Ag:SnO_2 films exhibited a broad emission peak at 536 nm (2.31 eV). The lowest electrical resistivity of 0.005 Ωcm was obtained at the films annealed at 500 ^{o}C. The optical studies show that the visible transmittance and band gap of the films increase with annealing temperature.

Keywords: A. Oxides, A. Thin films, C. X-ray diffraction

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*Corresponding author.

Tel: + 351 239 790745, Fax: +351 239 790701
E-mail address: albano.cavaleiro@dem.uc.pt (A. Cavaleiro)
akepati77@gmail.com (A.S. Reddy)

1. Introduction

In recent decades tin oxide (SnO_2) has attracted great attention in many applications such as solar cells, gas sensors, liquid crystal displays, optoelectronic devices, etc., because of its excellent electrical and optical properties, high exciton binding energy of 130 meV at room temperature, wide band gap (3.6 eV) and, additionally, its high chemical and thermal stability [1-4]. Recently, it was reported that the nanosized SnO_2 is a promising candidate for the sensitive and long-term stable detection of pollutant gases [5]. It is well know that the gas sensitivity depends on the electrical properties of the film and thus a precise control of the tin oxide microstructure is needed. The electrical resistivity of SnO_2 films is readily modified by the post deposition annealing or addition of dopants. An improvement in the sensitivity and selectivity and decrease in the working temperature for maximum sensitivity of the SnO_2 films was achieved by using suitable additives such as Ag, Pt, Pd, Cu, Ni, Au, Mn, In, etc.[6-9]. The nanocrystalline films and metal doped SnO_2 films have been synthesized by various approaches, such as atmospheric pressure chemical vapor deposition [10], electron beam evaporation [11], pulsed laser deposition [12], sol-gel [9], sputtering [8, 13], and electrostatic spray deposition [14]. Among these techniques, pulsed magnetron sputtering has recently become a very popular method of thin film deposition, due to its versatility, high stability, controllability, repeatability and ability to provide uniform coatings over large areas substrate up to 4 m in width [15,16]. In this work, pulsed magnetron sputtering technique was used to prepare Au:Ag doped SnO_2 films, and the effects of post annealing treatment on structural, compositional, surface morphology, electrical and optical properties of the films were studied in the view to achieve improved electrical and optical properties.

2. Experimental

The Au:Ag:SnO_2 films were deposited on cleaned glass substrates by pulsed magnetron sputtering using a Sn target (15cm x 15cm x 0.7cm, 99.99% purity) incrusted with high purity Au and Ag strips (99.999% of purity). The deposition was carried out in a reactive atmosphere in the presence of a mixture of pure Ar and O_2 gases, with a molar ratio Ar:O_2 of 0.5. The deposition pressure was fixed at approximately 0.7 Pa. The substrate holder was neither biased nor intentionally heated and it was set to a constant rotation speed of 20 r.p.m.. The target to substrate distance was fixed at 6 cm. Before deposition, an ultimate vacuum pressure better than 6×10^{-4} Pa was reached. The substrates surface was ion cleaned with an ion gun. The cleaning procedure first included an electron heating and afterwards an Ar+ bombardment, for 10 minutes each (ion gun settings at 20A, 40V and substrate bias progressively increased to -70V). During the deposition of the films, the power on the target was fixed at 900W, and the substrate was initially unheated. The thickness of the films, determined by profilometry, was approximately ~340 nm. The chemical composition of the coatings was determined by an electron probe microanalysis (EPMA) apparatus equipped with wavelength-dispersive X-ray spectroscopy (WDX). The structural properties of the films were determined by X-ray diffraction (XRD). The surface morphology was characterized by atomic force microscopy (AFM). The photoluminescence (PL) spectra were measured with a LS 55 fluorescence spectrometer (Perkin Elmer) at room temperature. The electrical properties of the films were measured by four point probe technique and the optical transmittance was recorded using a UV-Vis-NIR double beam spectrophotometer. The samples were annealed at 300, 400, and 500 ^{o}C in a horizontal furnace with protective atmosphere (95% Ar + 5% H_2). A heating rate of 30ºC/min and an isothermal period of 60 min was used. Then, the furnace was turned off and samples were let to cool down therein.

3. Results and Discussion

EPMA results show that the Au:Ag:SnO_2 films contain tin and oxygen, with a Sn/O ratio close to the stoichiometric compound SnO_2 (Table 1). The gold and silver incorporation in the films is approximately 0.6 and 0.3 at.%, respectively. After annealing the samples at 500ºC the oxygen content slightly diminished as a result of the annealing procedure. Due to the usage of protective atmosphere, desorption of oxygen is expected, especially in the grain boundaries and at the sub-surface of the grains.

Sample	Sn (%)	O (%)	Au (%)	Ag (%)	Sn/O
As deposited	32.3	66.8	0.6	0.3	0.48
500ºC	33.7	65.4	0.6	0.3	0.52

Table 1: Chemical composition of pulsed dc magnetron sputtered Au:Ag:SnO_2 films.

3.1. Structural and surface morphology

Figure 1 shows the XRD patterns of Au:Ag:SnO_2 films as function of annealing temperature. The films were polycrystalline with absence of impurity phases. It can be clearly observed that they all grew preferentially with the (110) orientation of SnO_2 with tetragonal structure (JCPDS Card No. 88-0287). The X-ray diffraction measurements did not reveal the presence of any Au or Ag phase, or their oxide phases, most probably Au and Ag atoms segregate to the noncrystalline region in the grain boundaries or are substitutionally incorporated into the tin oxide lattice. Considering the former case, the concentration of noble metal may have been too low to allow the formation of metal clusters with dimensions higher than the XRD limit of detection(>2-3 nm), even after annealing at 500ºC. The formation of metallic clusters with detectable sizes is expected at higher annealing temperatures. For example, Cabot et al. [17] observed the impregnation of SnO_2 crystals with Au, Pd and Pt and found that the formation of metallic clusters only occurred for samples annealed above 600ºC.

After post-deposition annealing, the width of the diffraction peaks decreased and the intensity of the (110), (101), (211) peaks increased. The improvement in the crystallinity of the Au:Ag:SnO_2 films with annealing temperature is a result of grains growth, which should be accompanied with a reduction of the microstructural defects and the consequent improvement in the structural homogeneity of the films. A shift in the diffraction angles towards higher values was also detected arising from the progressive contraction of the lattice parameters with the temperature increase. The lattice parameters *a* and *c* were calculated from the (110) peak and (211)/(110) peaks, respectively, and they are listed in Table2. A lattice distortion is observed when *a* and *c* values of the as deposited sample are compared with the equilibrium ones (#88-0287) or with literature concerning pure SnO_2 thin films [18], which reinforces the suggestion of Au and/or Ag being integrated in the SnO_2 lattice. The as deposited films may thus exhibit a large number of defects and local lattice disorder. Both lattice parameters decreased gradually with increasing annealing temperature; however, *c* parameter is always higher than the equilibrium value of SnO_2, whereas the *a* parameter is lower after 400ºC annealing. This results in an increased *c*/*a* ratio, irrespectively of the annealing temperature, when compared to equilibrium values. The changes in the lattice parameters with annealing temperature was due to the progressive removing of the lattice defects and to the structural re-arrangement of Ag:Au:SnO_2. The arising of compressive stresses during cooling down after thermal annealing should also contribute to the observed results.

Cetinorgu et al.[19] reported that the lattice parameters (*a* and *c*) increased with increasing annealing temperature from 400 to 600 ^{o}C, in filtered vacuum arc deposition SnO_2 films. However, Lee et al.[20] reported that the lattice parameters (*a* and *c*) decreased as the amount of manganese contents increases in Mn:SnO_2 ceramics.

The average crystallite sizes were calculated from the XRD spectrum by using Scherrer formula [21], and are listed in Table 2. As expected, the grain size of the films increases with the increase of the annealing temperature. Bazargan et al.[22] observed the increasing of the grain size with increase of annealing temperature in spin coated tin oxide films, and the crystallinity of the films started at 350 ^{o}C.

Sample	Annealing temperature (ºC)	Grain size (nm)	Lattice Parameters (Å)		c/a	Unit Cell Volume (Å^3)
			a	c		
Au:Ag:SnO_2	As deposited	5.4	4.757	3.232	0.679	73.14
	300	5.7	4.738	3.226	0.681	72.42
	400	7.3	4.719	3.207	0.680	71.42
	500	8.5	4.718	3.197	0.678	71.16
SnO_2 (#88-0287)	-	-	4.737	3.186	0.673	71.51

Table 2: Structural properties of the Au:Ag:SnO_2 sample at different temperatures

Figure 2 shows the surface morphology of as deposited and annealed Au:Ag:SnO_2 films. The grain growth with the annealing temperature is clearly evidenced by the AFM results. The as deposited films exhibited a rough surface with an average RMS roughness of 3.2nm. When increasing the annealing temperature from 300 to 500 ^{o}C the surface of the films changed significantly and the grains became bigger. The RMS roughness of the films is found to decrease with increasing of the post annealing temperature. The surface roughness decreases as a result of the grains growth. From the AFM histograms, we obtained the grain size of the as deposited and annealed Au:Ag:SnO_2 films, listed in Table 3. With the increase in the annealing temperature bigger grains were observed, as a result of the increased crystallinity (Fig.1). The grain sizes obtained from the AFM histograms are slightly higher than those measured from XRD data, which might suggest the formation of surface aggregates, originated by the lateral growth of the grains, contributing to the improvement in the smoothness of the films.

Sample	RMS roughness (nm)	Grain Size (nm)
As deposited	3.2	8
300°C	2.9	10
400°C	2.4	11
500°C	2.1	13

Table 3 surface roughness and grain size values from AFM analysis

3.2. Photoluminescence properties

Photoluminescence (PL) studies provide information regarding the quality of the film. The annealing temperature strongly affected the emission properties of the Au:Ag:SnO_2 films. Fig.3 shows the room temperature PL spectra of the Au:Ag:SnO_2 films. The films did not exhibit luminescence peaks in the UV region (not shown in Fig.3). The as deposited Au:Ag:SnO_2 films exhibited a broad emission peak at 536 nm (2.31 eV). After annealing, a main emission peak in the same position and with growing intensity with temperature was observed, and an additional shoulder peak appeared after 400ºC at 602 nm (2.06 eV). In poly- and nano-crystalline oxides, oxygen vacancies are the most common defects and usually act as radiative centers in luminescence processes [23]. Considering the results of the chemical composition, higher amounts of oxygen vacancies are expected for the annealed samples, despite the films crystallinity increase, which can justify the PL emissions increase. The very low cooling rates used after the annealing process can affect the distribution of space charges in the nanoparticles with a vacancy migration from the bulk to the surface of the grains [24]. In this way, despite the bigger and more ordered grains (with less "bulk" defects), more oxygen vacancy defects in the near-surface region are expected. The presence of noble metal dopants can also influence the PL performance of semiconductor nanomaterials. Although the noble metal cannot result in new PL phenomena, it can make the excitonic PL intensity decrease due to the capture of noble metal ions (resulting in increased separation rates of photo-induced charge carriers) [25]. Although a

very high density of defects is expected in the as deposited film due to the tin oxide doping by Au and Ag, the very low PL signal indicates a very low concentration of oxygen vacancies but can also indicate the presence of noble metals in the ionic form (i.e. Au and/or Ag integrated in the oxide Sn lattice). At the lower annealing temperature of 300ºC the intensity of the PL peak increases very slightly, maintaining the same broad shape of the as deposited sample. Although the amount of energy was probably not sufficient to induce significantly the structural re-arrangement of the Au:Ag:SnO_2 films, an increase in the surface oxygen vacancies would be expected due to the annealing procedure. Once again, the presence of noble metal ions could be responsible for the very low PL intensity increase due to the efficient separation of photoelectrons and holes. The very broad PL peaks in both the as deposited and 300ºC annealed samples also indicates the presence of defects with slightly different energy levels, which might be connected with the presence of different ionic noble metal species. With further increase in the annealing temperature the main PL emission peak is sharply increased in intensity due to an increase in the surface oxygen vacancies concentration, and this also indicates that the noble metal atoms should be less in their ionic form. Their precipitation near the grain boundaries can in fact contribute to higher PL signals by the creation of recombination centers.

Ni et al. [26] observed the decreasing of the peaks intensity at too low and too high annealing temperatures in rf magnetron sputtered Sb doped SnO_2 thin films. Zhang et al. [27] observed a decrease of the green-yellow emission and an increase of the UV emission with increase of silver content in Ag/ZnO composites.

3.3. Electrical properties

In transparent conducting oxides, native defects, such as O vacancies and cation interstitials, have been frequently invoked as possible sources of n-type conductivity. The conductivity of the SnO_2 films results mainly from stoichiometric deviation, such as excess metal

ions and/or oxygen vacancies. It can be seen that the electrical resistivity of the films was significantly changed by the annealing temperature (Table 4). The as deposited film exhibited the higher value of resistivity. This should be related to the excess of oxygen chemisorbed at grain boundaries and also to the presence of structural defects inside the grains other than oxygen vacancies. The resistivity of the films was sharply decreased after thermal treatments. This was an expected result mainly due to the increase of grain size and of structural homogeneity and to the reduction of scattering of carriers at the grain boundaries with annealing temperature but can also be connected to the decrease of excess oxygen and/or to the increase of oxygen vacancies (which in turn leads to an increase of the carrier concentration) [28,29]. Additionally, the dopants depletion from the SnO_2 lattice and subsequent clusterization at the grain boundaries can also contribute for decreasing the resistivity of the film since the ionic metals can act as trapping centers.

Sample	Resistivity (Ωcm)	Transmittance (%) at λ=575	Band gap (eV)
as deposited	15.8	84	3.11
300 ^{o}C	1.3	85	3.12
400 ^{o}C	0.06	87	3.14
500 ^{o}C	0.005	89	3.19

Table 4 Electrical and optical properties of Au:Ag:SnO_2 films

3.4. Optical properties

The optical transmittance of the films was strongly influenced by the annealing temperature. The transmittance of the films gradually increased in the visible region (at λ=575 nm) and decreased in the near infrared region with the annealing temperature from as deposited to 500 ^{o}C. The enhancement of transmittance in the visible region with annealing temperature may be due to a decrease in optical scattering caused by the densification of grains followed by the grain growth and the reduction of the grain boundary density [30]. The optical properties of

thin films was also found to be influenced by the surface morphology, the smoother surface morphology and less grain boundary the film has, the higher the transmittance [31]. The absorption edge of the Au:Ag:SnO_2 films is shifted to shorter wavelengths with the increase in the annealing temperature, ascribed to increasing the optical band gap. The optical band gap of the films increases from 3.11 eV to 3.19 eV with the increase in the annealing temperature (Table 4). The results in the literature vary depending on the deposition and posterior annealing treatment. A similar behavior was reported by Huanga et al. [32] for rf reactive magnetron sputtered antimony tin oxide films. The absorption edge shifted towards shorter wavelengths with the increase in the annealing temperature due to an improvement in the crystallinity of the films and higher concentration of carriers. Cetinorgu et al. [19] observed an increase of optical band gap from 3.90 to 4.35 eV with an increase of the annealing temperature from as deposited to 600 ^{o}C in vacuum arc deposited SnO_2 films.

Conclusion

Nanocrystalline Au:Ag:SnO_2 thin films were prepared on glass substrates by using pulsed d.c. magnetron sputtering and further annealed in order to improve their opto-electrical properties. The studies show remarkable changes in the properties of the films with respect to the annealing temperature. XRD and AFM results show that the crystallinity, homogeneity, and smoothness of the films improved with annealing temperatures. In the PL spectra, a broad emission peak located at 536 nm (2.31 eV) was detected, and after annealing its intensity was sharply increased and an additional shoulder peak appeared at 602 nm (2.06 eV). The resistivity of as deposited films was greatly decreased after annealing at higher temperatures. With the increase in the annealing temperature the optical transmittance increased from 84% to 89% and the absorption edge was moved to shorter wavelength direction.

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References

[1] A. Dieguez, A. R-Rodriguez, J.R. Morante, U. Weimar, M. S-Berberich, W. Gopel, Sens. Actuators B 31 (1996) 1-8.
[2] T. Seiyama, A. Kato, K. Fujishima, N. Nagatani, Anal. Chem. 34 (1962) 1502–1503.
[3] M. Batzill, U. Diebold, Prog. Surf. Sci. 79 (2005) 47-154.
[4] B. Yu, C. Zhu, F. Gan, Opt. Mater. 7 (1997) 15-20.
[5] K.D. Schierbaum, U. Weimar, W. Goepel, Sens. Actuators B 7 (1992) 709-716.
[6] O.V. Safonova, M.N. Rumyantseva, R.I. Kozlov, M. Labeau, G. Delabouglise, L.I. Ryabova, A.M. Gaskov, Mater. Sci. Eng. B 77 (2000) 159-166.
[7] C. Jin, T. Yamazaki, K. Ito, T.Kikuta, N. Nakatani, Vacuum 80 (2006) 723–725.
[8] A. Espinosa, N. Menéndez, C. Prieto, A. de Andrés, J. Non-Crystalline Solids 354 (2008) 5269–5271.
[9] I. Fasaki, M. Suchea, G. Mousdis, G. Kiriakidis, M. Kompitsas, Thin Solid Films 518 (2009) 1109–1113.
[10] R. Karslıo˘glu, M.Uysal, H.Akbulut, J. Crystal Growth 327 (2011) 22–26.
[11] V. Senthilkumar, P. Vickraman, J Mater Sci: Mater Electron 21 (2010) 578–583.
[12] E. Fazio, F. Neri, R. Ruggeri, G. Sabatino, S. Trusso, G. Mannino, Applied Surface Science 257 (2011) 2520–2525.
[13] Y. Shen, T. Yamazaki, Z. Liu, D. Meng, T. Kikuta, Thin Solid Films 517 (2009) 6119–6123.
[14] C.M. Ghimbeu, M. Lumbreras, M.Siadat, R. C. van Landschoot, J. Schoonman, Sens. Actuators B 133 (2008) 694–698.
[15] J. O'Brien, P.J. Kelly, Surf. Coat. Technol. 142-144 (2001) 621-627.
[16] W.M. Posadowski, Thin Solid Films 343-344 (1999) 85-89.
[17] A. Cabot, J. Arbiol, J.R. Morante, U. Weimar, N. Barsan, W. Gopel, Sensors and Actuators B 70 (2000) 87-100.
[18] Z.W. Chen, J.K.L. Lai, C.H. Shek, Phys. Rev. B 70 (2004) 165314-7.
[19] E.Cetinorgu, S. Goldsmith, Yu Rosenberg, R.L. Boxman, J. Non-Crystalline Solids 353 (2007) 2595-2602.

[20] C-H. Lee, Bo-Ae Nam, W-K.Choi, J.-K. Lee, D.-J. Choi, Y.-J. Oh, Materials Letters 65 (2011) 722-725.
[21] B. D. Cullity, Elements of X-ray Diffraction, second ed., Addison Wesley, London.
[22] S. Bazargan, N.F. Heinig, D. Pradhan, K.T. Leung, Cryst. Growth Des. 11 (2011) 247- 255.
[23] F. Gu, S.F. Wang, C.F. Song, M.K. Lu, Y.X. Qi, G.J. Zhou, D. Xu, D.R. Yuan, Chemical Physics Letters 372 (2003) 451-454.
[24] J. Liu, S. Gong, L. Quan, Z. Deng, H. Liu, D. Zhou, Sensors and Actuators B 145 (2010) 657–666.
[25] J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Baojiang, Y. Libin, F. Wei, F. Honggang, S. Jiazhong, Solar Energy Materials & Solar Cells 90 (2006) 1773-1787.
[26] J. Ni, X. Zhao, X. Zheng, J. Zhao, B. Liu, Acta Materialia 57 (2009) 278–285.
[27] Y. Zhang, J. Mu, J. Collo. Interf. Sci. 309 (2007) 478-484.
[28] J.H. Lee, K.H. Ko, B.O. Park, J. Cryst. Growth 247 (2003) 119–125.
[29] R.C. Scott, K.D. Leedy, B. Bayraktaroglu, D.C. Look, Y.H. Zhang, Appl. Phys. Lett. 97 (2010) 072113.
[30] H. Li, J. Wang, H. Liu, H. Zhang, X. Li, J. Cryst. Growth 275 (2005) e943-e946.
[31] N. Bouhssira, S. Abed, E. Tomasella, J. Cellier, A. Mosbah, M.S. Aida, M. Jacquet, Applied Surface Science 252 (2006) 5594-5597.
[32] J-L. Huang, Y. Pan, J. Y. Chang, B-S. Yau, Surf. Coat. Technol. 184 (2004) 188–193.

Figure captions

Figure 1. XRD patterns of Au:Ag:SnO_2 films as function of annealing temperature

Figure 2. AFM images of Au:Ag:SnO_2 films (a) as deposited, (b) 300 ^{o}C, (b) 400 ^{o}C, (b) 500 ^{o}C.

Figure 3. Room temperature PL spectra of Au:Ag:SnO_2 films

Figure 4. Optical transmittance spectra of Au:Ag:SnO_2 films as function of annealing temperature.

- The nanocrystalline Au:Ag:SnO_2 films were prepared by pulsed direct current magnetron sputtering
- After annealing, the homogeneity and smoothness of the films was improved.
- The low electrical resistivity of 0.005 Ωcm with optical transmittance of 89% were obtained at annealing temperature of 500 ^{o}C

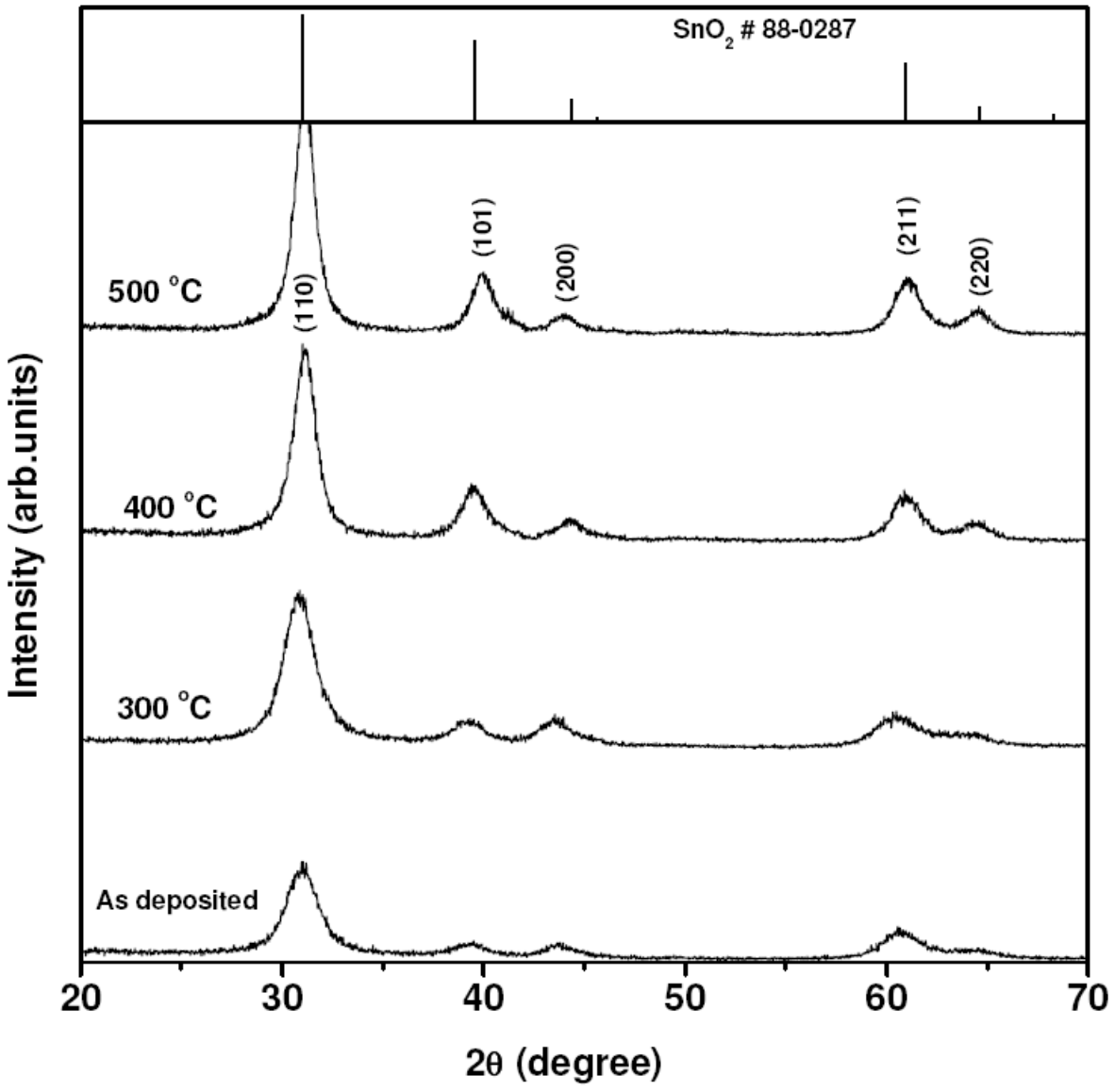

Fig.1

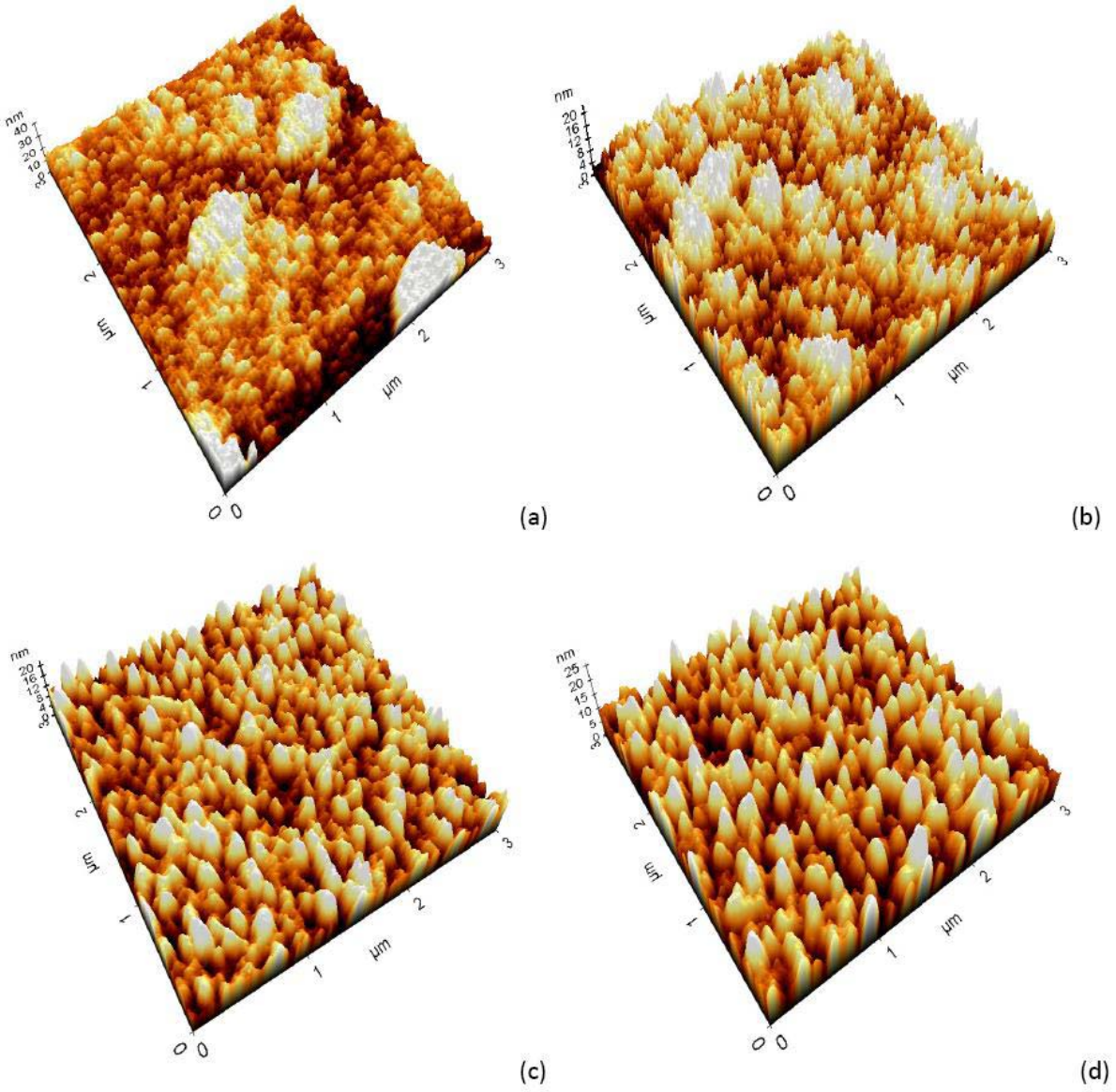
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Fig.2

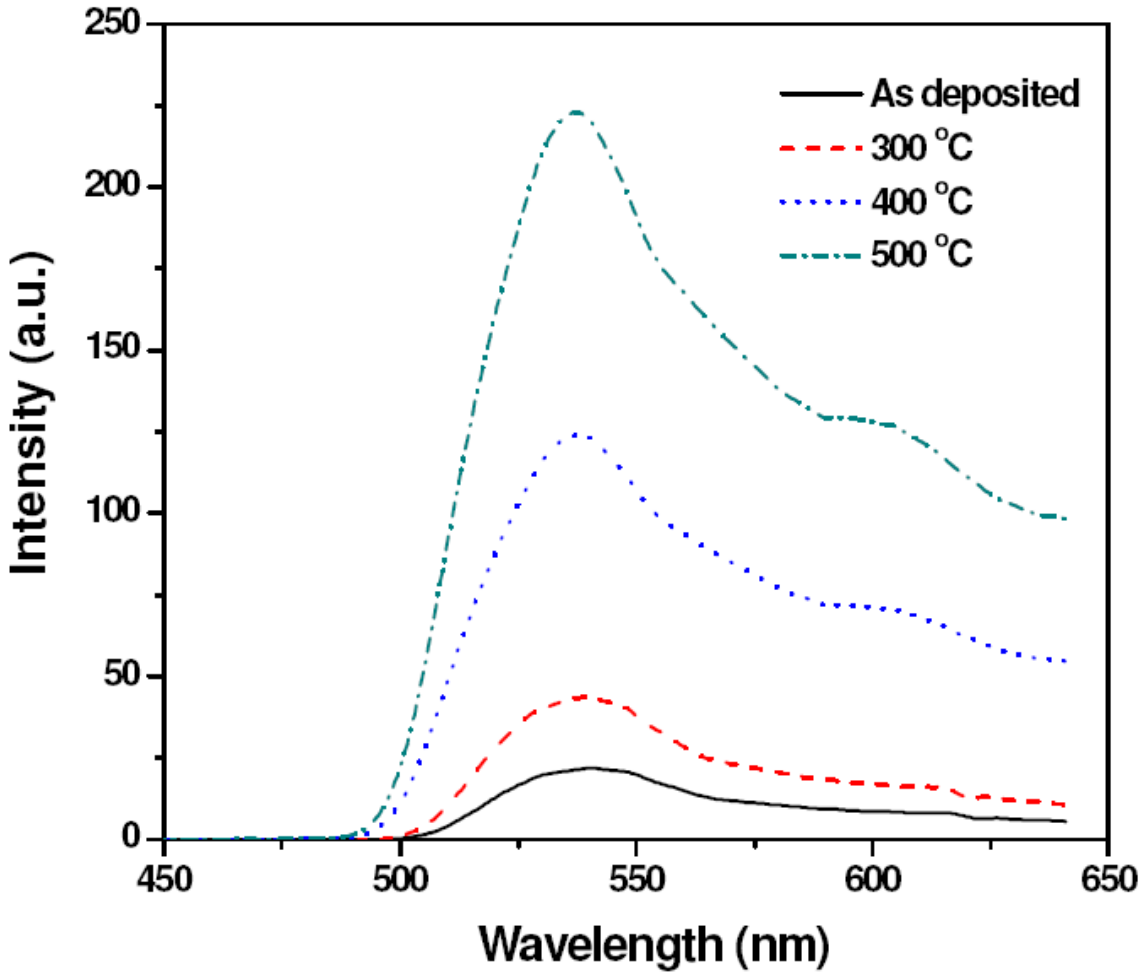
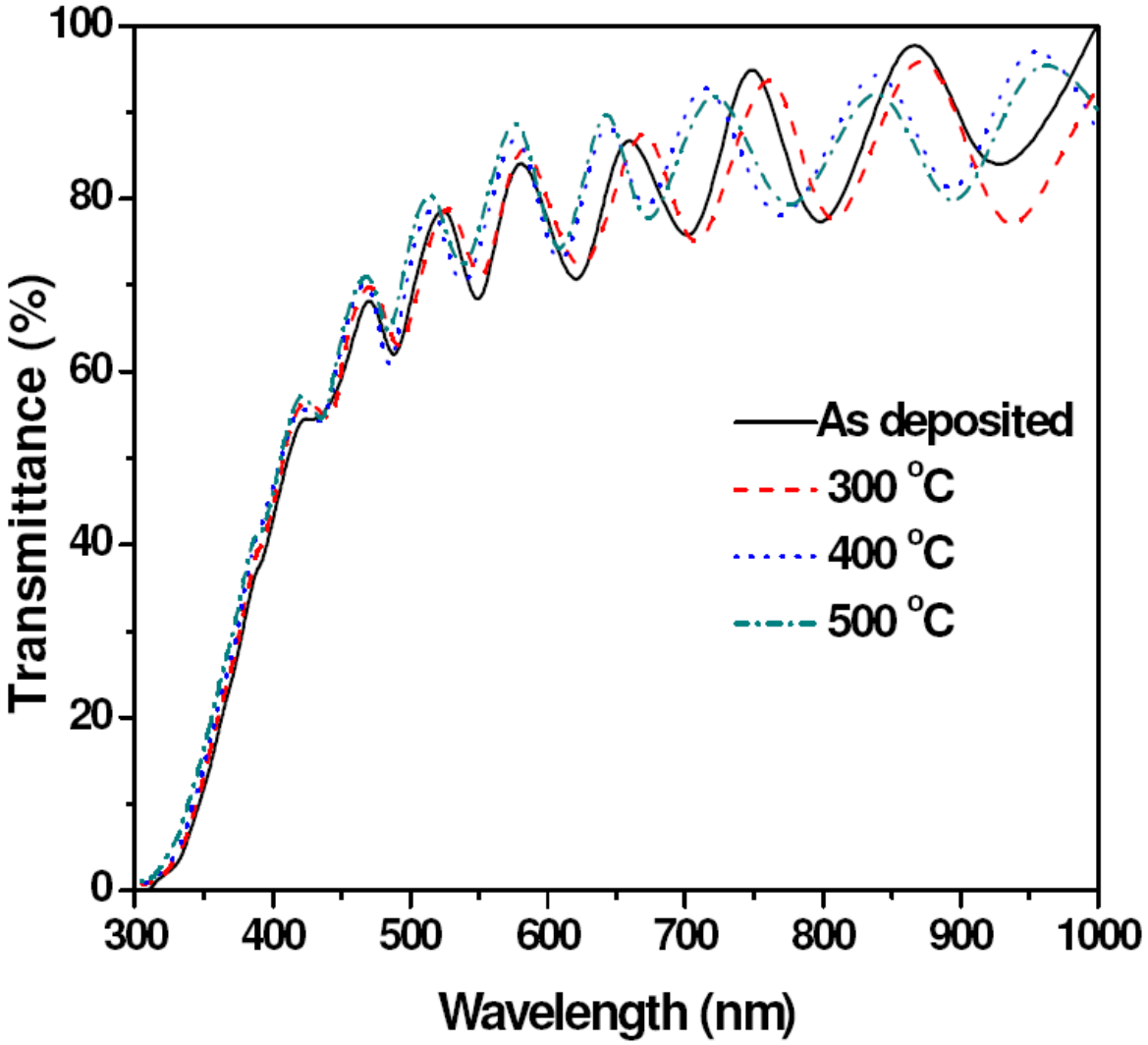


Fig.3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Transmittance (%)
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Wavelength (nm)
As deposited
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400 °C
500 °C

Fig.4