Morphological and structural studies of WO_x thin films deposited by laser ablation

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Abstract
Tungsten oxide is an interesting compound with many applications in gas sensors, electrochromic and photochromic devices. Thin films of tungsten oxide were obtained by pulsed laser deposition (PLD) and Radio Frequency assisted PLD (RF-PLD). A tungsten target was ablated in reactive oxygen atmosphere (0.01-0.05 mbar). The deposition parameters such as laser fluence, substrate temperature, radiofrequency power were varied, while different materials (Corning Glass and Silicon) have been used as substrates. The obtained films showed good adhesion to the substrate and uniform surface aspect, which are important properties for applications. X-ray diffraction, Auger Electron, Raman Spectroscopies and Atomic Force Microscopy were used for characterization.

Introduction

Tungsten oxide is a wide band gap semiconductor metallic oxide. Thin films of tungsten oxide are interesting for applications as active layer in gas sensors: WO_3 was used to detect gases such as H_2S and H_2, small concentrations of NO and Cl_2. It was demonstrated to have applications as catalyst, in window for solar cells, electronic information displays and color memory devices [1-5]. Thin films of tungsten oxide can be fabricated by different vacuum deposition methods; having high melting and boiling temperature, special energetic requirements have to be fulfilled to evaporate it. Pulsed Laser Deposition allows the local heating, evaporation and plasma formation of W target in oxygen atmosphere and compound formation in the form of thin film. In this work the properties of WO_x films obtained by Pulsed Laser Deposition (PLD) and Radio Frequency assisted PLD (RF-PLD) are analysed.

Experimental

A metallic Tungsten target was ablated in reactive atmosphere of oxygen at pressures ranging from 0.01 mbar to 0.05 mbar. The beam of a frequency-tripled SURELITE II Nd: YAG laser (wavelength 355 nm, pulse length 5 ns, repetition rate 10 Hz) was focused through a spherical lens on the target at 45^{o} incidence. The laser fluence was in the range of 4–8 J/cm^2. In order to achieve uniform ablation, the target was simultaneously rotated and translated. (100)-Silicon and Corning glass were used as substrates. The substrates were positioned at 4 cm in front of the target, parallel to it. The temperature of the substrates was varied between RT and 600^0C. The deposition parameters are summarised in table 1.

A major problem for oxides thin films is the appearance of oxygen vacancies both inside the layer and at the layer-substrate interface. The use of a hybrid technique combining the advantages of conventional PLD (clean reactor, low temperature and high efficiency process) with "in situ" enhancement of the reactivity on the substrate overcomes the above problem. In our experiments the substrate reactivity is increased as a result of addition to the PLD set-up of an excited and/or ionized beam of oxygen atoms and molecules produced by the radio-frequency discharge.

The plasma beam source consists of a double chamber discharge system equipped with a radio-frequency (13.56 MHz, CESAR 1310, RF maximum power 1000 W) power supply. In the active chamber, the discharge is generated in flowing oxygen between two parallel electrodes (16 mm diameter). It expands into the ablation chamber as a plasma beam, through an aperture (~2 mm diameter) drilled in the bottom electrode, which acts as a nozzle [6]. In figure 1 is shown the experimental set-up.

Atomic Force Microscopy, X-ray diffraction and reflectivity, Auger Electron Spectroscopy and Raman Spectroscopy were used for layers characterization.

The aim of this work is to find the best conditions for growing nanocristalline films of WO_x that can be suitable candidates for miniaturized gas sensor fabrication.

Results and discussions

The influence of different experimental parameters as RF power, substrate temperature or laser fluence on the WOx layers properties was studied.

Atomic Force Microscopy studies evidenced that the rf beam addition strongly influences the surface morphology. Thus, sample w621 prepared with RF discharge addition had a better morphology than sample w619 deposited in the same conditions, without RF. On a 20×20 μm^2 scale, the surface of thin films deposited by RF-PLD is more compact, without droplets and with a smaller roughness, around 1 nm (fig. 2). Simultaneously, the RF addition results in the diminishing of layers grain size.

The substrate temperature was also found to play an important role in the film morphology. Even if the roughness has (small) close values for all layers, the general aspect is completely different. A dense, droplets and cracks free film was obtained at 400 ^{0}C substrate temperature (Fig. 3b). For 200 °C substrate temperature clusters with diameter larger than 500 nm appeared on the film surface, while at 600 ^{0}C the film became porous (fig.3).

Another parameter which influences the morphology of the thin films is laser fluence. It was observed that decreasing the laser fluence from 8J/cm^2 to 3 J/cm^2, the quality of the film surfaces was improved, becoming more compact, without droplets and with lower roughness and porosity (fig. 4).

Film composition was investigated by Auger Electron Spectroscopy (AES), with an AES-3017 spectrometer. It was noticed that for thin films grown at 200 ^{0}C and 400 ^{0}C, the ratio of atomic concentrations W:O is almost 1:1 (the atomic concentrations of samples w83 and w91 are W 51.3%, O 48.7% and W 53.49%, O 46.51 %, respectively). Increasing the temperature to 600 ^{0}C, the ratio of W:O became smaller (for sample w92 was recorded a W:O ratio of 38.5% : 61.5%). This decrease can suggest the appearance of either a WO_{3-x} compound or a $WO+WO_3$ mixture.

The XRD patterns were recorded on a DRON DART UM-2 diffractometer equipped with a Cu anode and a graphite monochromator in the diffracted beam in a Bragg – Brentano geometry. Scans were acquired with a step size of 0.05^0 with an acquisition time on each step of 2s. Although the X-ray patterns did not show any peak related to the formation of crystalline WO_x , we can speculate that nanocrystallites with very small dimensions are present in our layers.

The deposited films grown on Corning glass were studied in micro-Raman configuration. The 514 nm line of an Ar^+ laser was focused on the sample by a 50x Leica Germany optical objective (NA = 0.75 corresponding to 0.5 µm nominal spot diameter for the excitation wavelength employed). The highest laser power used was 0.5 mW with the aim to avoid local annealing and photo-induced structural modifications. The backscattered light was collected by the same objective and analyzed by a Renishaw inVia Raman Microscope equipped with a holographic Notch filter (cutoff at 100 cm^{-1}), a 1800 lines/mm diffraction grating and a thermoelectrically cooled RenCam CCD detector. In fig.5 are collected the Raman spectra of all examined films. Looking at the spectra an evolution is observed from metallic tungsten (w71) to amorphous tungsten oxide (w72), associated to the operation of RF power. The spectrum of w72 sample is characterized by two broad bands, the first one at low frequency in the range 100-500 cm^{-1}, associated to O-W-O bending modes, and the second one at 600-1000 cm^{-1}, in the W-O stretching frequency range. We notice that the latter band includes two features, the first around 800 cm^{-1} ascribed to W-O stretching vibration and the second around 950 cm^{-1} due to W=O stretching vibration, usually associated to the development of a nanostructure in the film [7]. These bonds are mainly located at the surface so that an intensity increase of the corresponding band indicates a high surface to volume ratio.

Preliminary X-Ray Reflectivity measurements [8], using monochromatic x-ray source at λ = 0.13926 nm ($Cu_{K\beta}$) on sample w72 permitted, from the position of the critical angle θ_c, to get a density value of 6.48 g cm^{-3}, which is close to WO_3 bulk density value (7.2 g cm^{-3}). We recall that θ_c is related to material density ρ through

$$\theta_c = \lambda\left[\frac{N_A r_0}{\pi}\rho\frac{Z+f'}{A}\right]^{1/2}, \qquad (1)$$

where N_A is the Avogadro's number, r_0 is the Thomson scattering length, f' is the dispersive correction factor, Z and A are the atomic and mass number of the material respectively.

When we move to samples w90 and w91 a separation between the two high frequency components begins, being probably related to the higher substrate temperature (400°C) in both films. The increased RF power at which sample w91 was deposited does not significantly affect the features of Raman spectrum. The spectra of samples w92 and w95 show a definite trend towards crystallization, as evidenced by a progressive definition of the W-O stretching bands at about 800 cm^{-1}. The dramatic role of substrate temperature T_s is highlighted by comparing the spectra of samples w91 (T_s, 400°C) and w92 (T_s, 600°C). When we compare the spectra of sample w91 and w95 the effect of laser fluence emerges. Decreasing the laser fluence, results in increased film crystallinity with a similar effect to increasing T_s. In fact a lower fluence coincides with a reduced plume expansion, in turn favoring cluster synthesis *in* the plume during its flight.

Conclusions

We have demonstrated the growth of WO_x layers with high WO_3 content by radiofrequency assisted pulsed laser deposition. Parameters like temperature and laser fluence have a big impact on film crystallinity and roughness. It was observed that the decrease of the laser fluence results in increased film crystallinity with a similar effect while increasing the substrate temperature. Nevertheless, the use of a higher temperature (600°C) leads to the appearance of pores on the film's surface. Under the investigated experimental conditions, the best WO_x films were obtained on Corning glass at 3 J/cm^2, 400 ^0C and 150 W power of RF discharge. Controlling the experimental parameters a nanocrystalline structure, an amorphous layer or an uniform and compact layer with large grains (180 nm-200 nm) can be obtained.

References:

[1] Ashirt P V, Bader G and Truong V-V 1998 *Thin Solid Films,* **320** 324

[2] Xu Z, Vetelino J F, Lec R and Parker D C 1990 *J. Vac. Sci.,Technol.* A **8** 3634

[3] Tagtstrom P and Jansson U 1999 *Thin Solid Films* **352,** 107

[4] Haro-Poniaowski E, Jouanne M and Morhange J F 1998 *Appl. Surf. Sci.* **127–9** 674

[5] Lee S H, Cheong H M, Edwin C, Pitts J R and Deb S K 2000, *Appl. Phys. Lett.* **76** 3908

[6] G. Dinescu, B.Mitu, E. Aldea, M. Dinescu, Vacuum, **56**, (2000), 83

[7] M. Boulova and G. Lucazeau, J. Sol. St. Chem., 167 (2002) 425

[8] V. Holy, U. Pietsch, T. Baumbach, Springer, Berlin, (1999)

Table 1

Sample	Substrate	P_{oxygen} (mbar) during deposition	T_{substr} (^0C)	N_{Pulse}	Φ_{laser} (J\cm^2)	P_{RF} (W)
71	Corning Glass	0.01	20	15.000	4.5	0
72	Corning Glass	0.01	20	15.000	4.5	100
83	Corning Glass	0.05	200	15.000	4.5	150
90	Corning Glass	0.05	400	12.000	4.5	100
91	Corning Glass	0.05	400	12.000	4.5	150
92	Corning Glass	0.05	600	12.000	4.5	150
94	Corning Glass	0.05	400	12.000	8	150
95	Corning Glass	0.05	400	12.000	3	150
619	Si (100)	0.05	20	15.000	4	0
621	Si (100)	0.05	20	15.000	4	150

Figure captions:

Fig.1 The PLD-RF system used to obtain thin films of WO_x

Fig.2 AFM images for sample deposited in the same condition but with different RF power a) 0 W and b) 150 W

Fig. 3 AFM images for samples deposited in the same conditions but at different temperatures a) 200 ^{0}C, b) 400^{0}C and c) 600 ^{0}C

Fig. 4 AFM images for sample deposited in the same conditions but with different laser fluences a) 8.28 J/cm^2, b) 4.5 J/cm^2, c) 3 J/cm^2

Fig. 5 Raman spectra for samples w71, w72, w90, w91, w92, w95

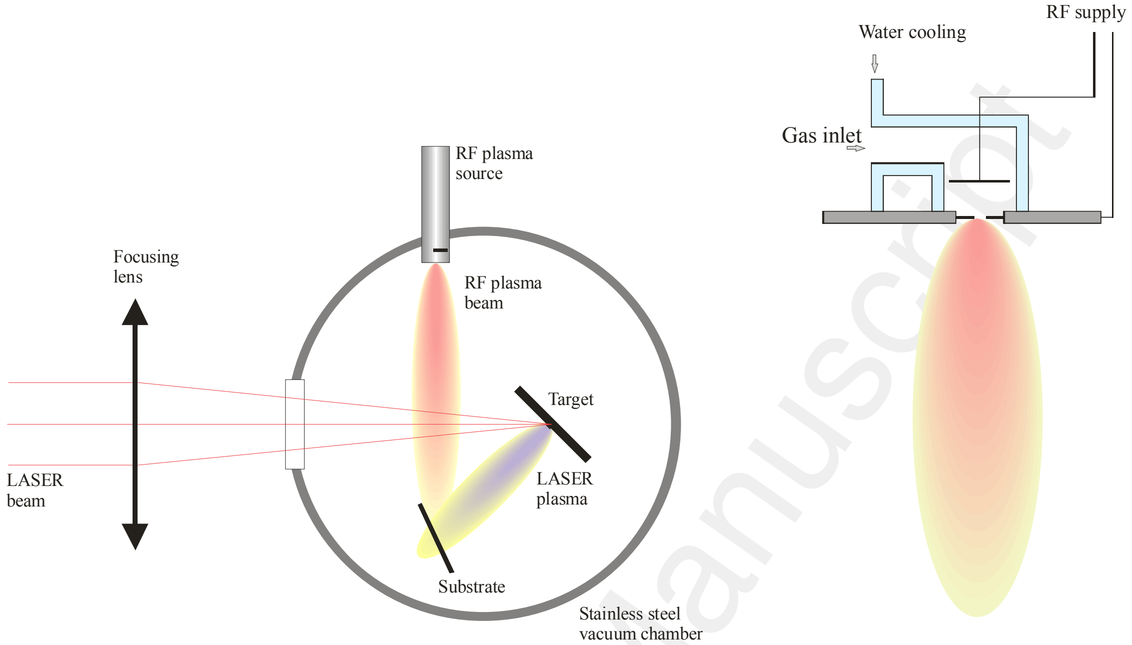

Focusing lens
LASER beam
RF plasma source
RF plasma beam
Target
LASER plasma
Substrate
Stainless steel vacuum chamber
RF supply
Water cooling
Gas inlet

Figure 1

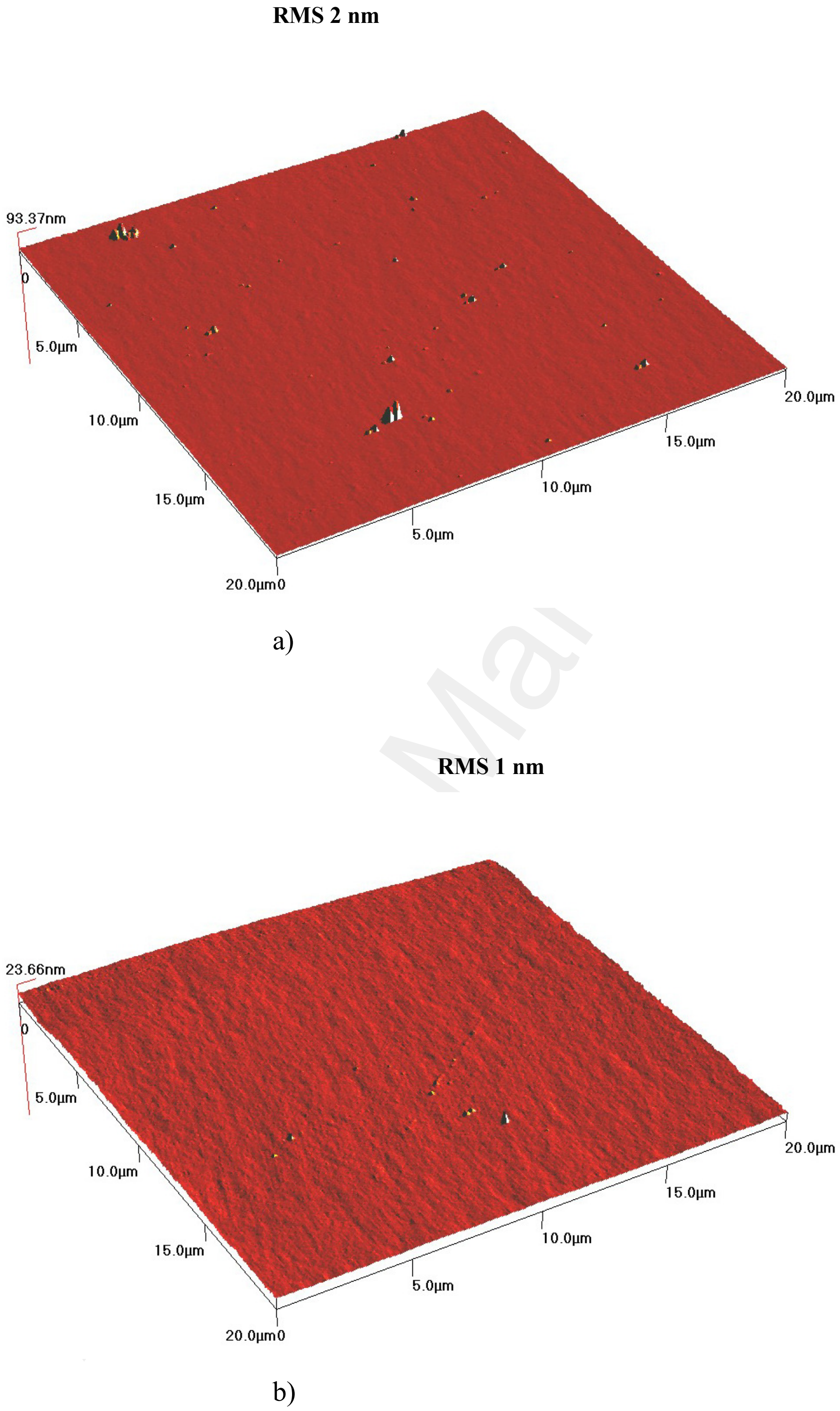

RMS 2 nm
93.37nm
0
5.0µm
10.0µm
15.0µm
20.0µm0
5.0µm
10.0µm
15.0µm
20.0µm
a)
RMS 1 nm
23.66nm
0
5.0µm
10.0µm
15.0µm
20.0µm0
5.0µm
10.0µm
15.0µm
20.0µm
b)

Figure 2

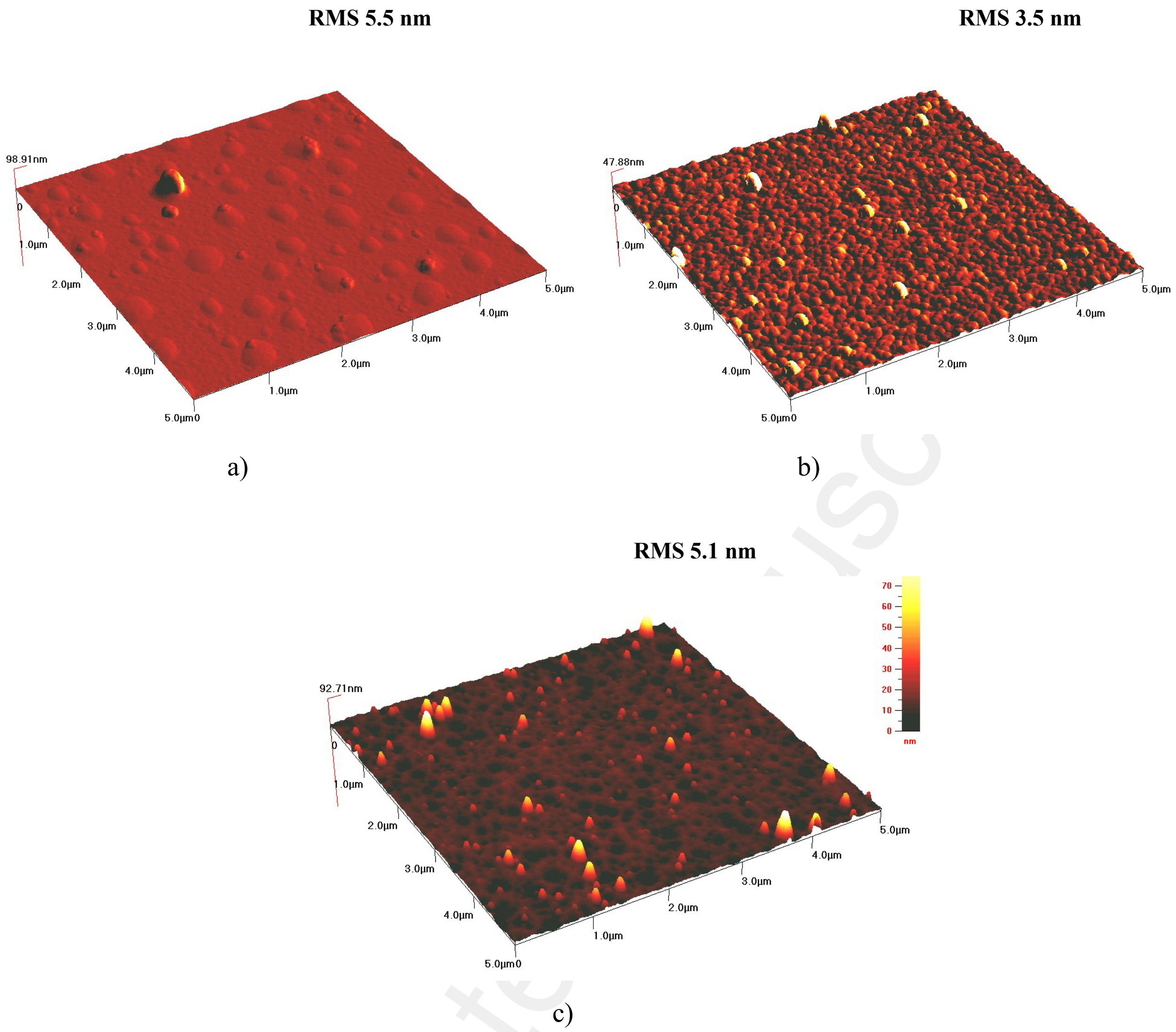
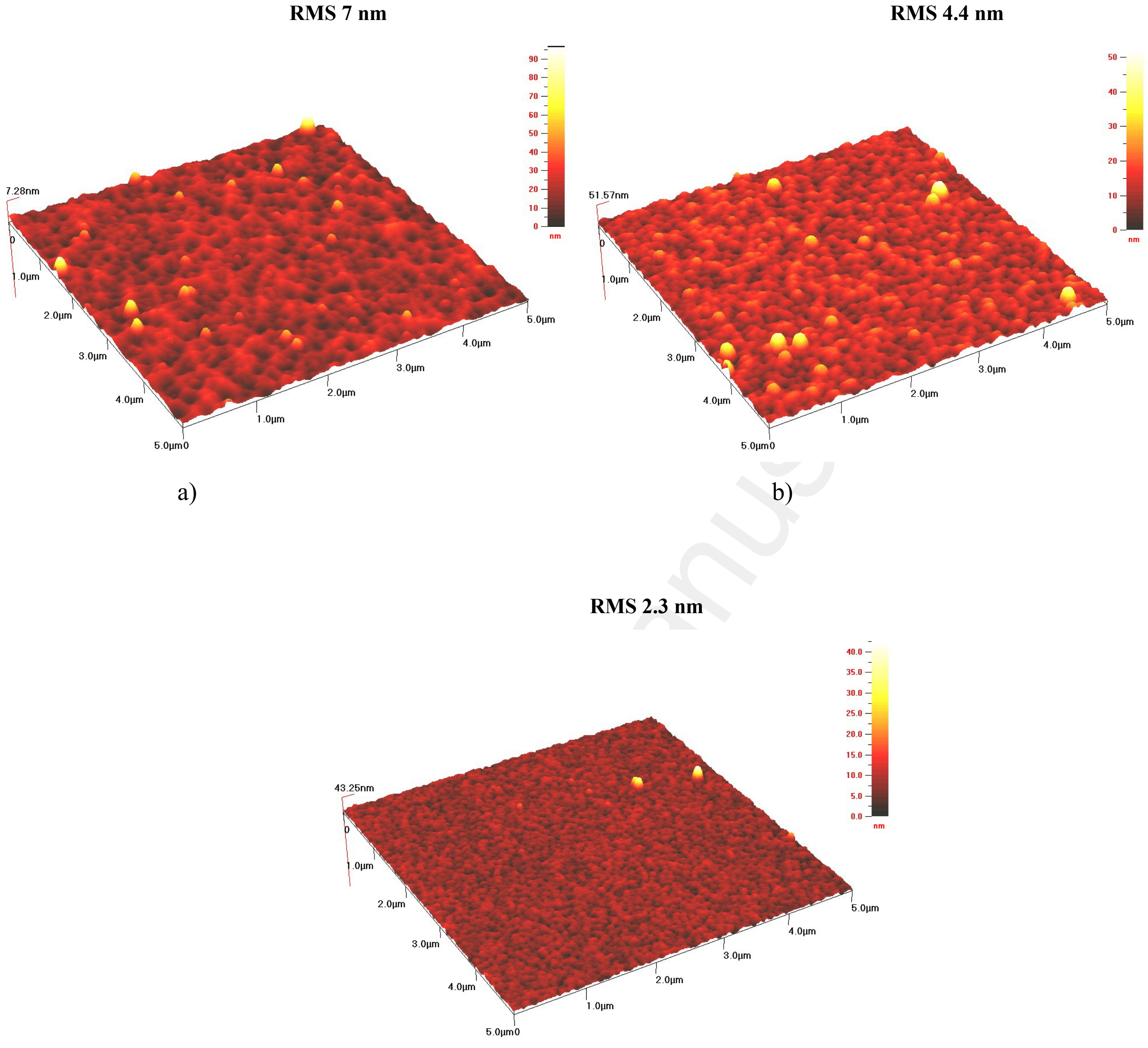

RMS 5.5 nm
98.91nm
0
1.0µm
2.0µm
3.0µm
4.0µm
5.0µm
5.0µm0
1.0µm
2.0µm
3.0µm
4.0µm
a)
RMS 3.5 nm
47.88nm
0
1.0µm
2.0µm
3.0µm
4.0µm
5.0µm
5.0µm0
1.0µm
2.0µm
3.0µm
4.0µm
b)
RMS 5.1 nm
92.71nm
0
1.0µm
2.0µm
3.0µm
4.0µm
5.0µm
5.0µm0
1.0µm
2.0µm
3.0µm
4.0µm
70
60
50
40
30
20
10
0
nm
c)

Figure 3



RMS 7 nm

a)

RMS 4.4 nm

b)

RMS 2.3 nm

c)

Figure 4

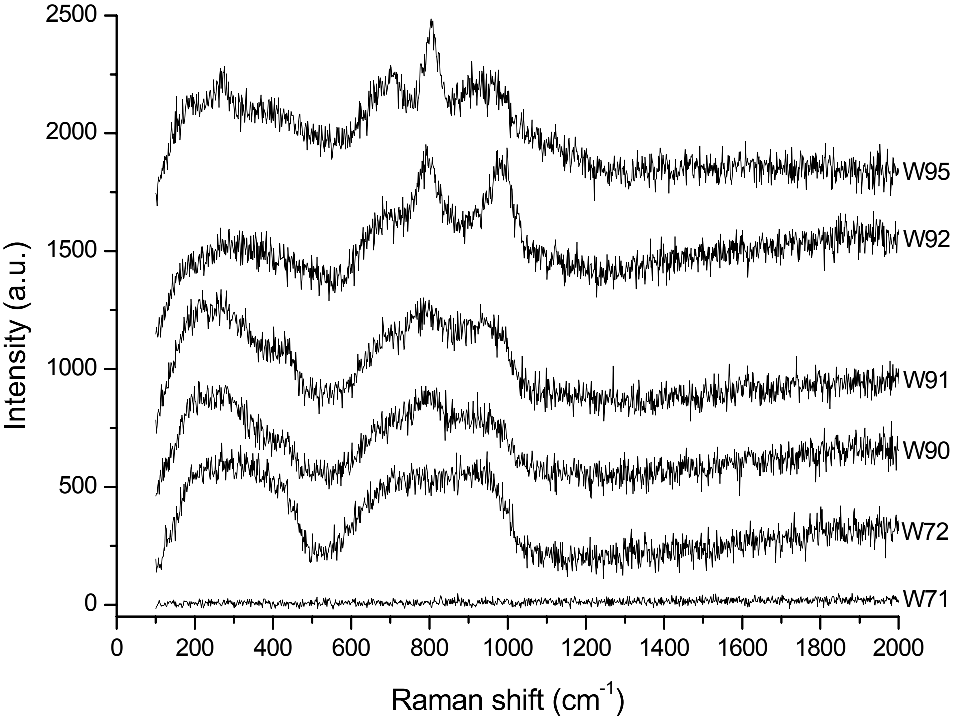

Intensity (a.u.)
2500
2000
1500
1000
500
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Raman shift (cm^{-1})
W95
W92
W91
W90
W72
W71

Figure 5