Article

Influence of GLAD Sputtering Configuration on the Crystal Structure, Morphology, and Gas-Sensing Properties of the WO₃ Films

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Abstract: In this paper, we describe a deposition method and investigation of the physical properties of WO₃ films. We investigated tungsten oxide due to its potential application as a gas sensor. Thin films of the WO₃ were deposited on glass, silicon, and alumina substrates by magnetron GLAD sputtering. The crystallinity of films was determined by X-ray diffraction (XRD) and the thickness by X-Ray Reflectivity (XRR) and spectroscopic ellipsometry (SE). Surface morphology, which is important for gas sensitivity, was measured by atomic force microscopy (AFM). We studied the gas-sensing characteristics under exposure to acetone in the 0.1–1.25 ppm range which covers the levels of exhaled breath acetone. We show that WO₃ sensors have different sensitivity for different sputter angle. Furthermore, we demonstrate the influence of temperature during gas content measurement.

Keywords: gas sensors; thin films; GLAD sputtering; tungsten oxides; acetone detection

1. Introduction

Tungsten oxide is a well-known semiconductor with a rich phase diagram, including WO₂, W₁₈O₄₉, W₂₄O₆₈, WO₃, and a series of nonstoichiometric WO_{3-x} [1]. Tungsten trioxide forms many different polymorphic phases, i.e., monoclinic, triclinic, orthorhombic, tetragonal, cubic, as well as hexagonal [2,3]. The WO₃ compound is built from a corner shared octahedrons of a W–O₆, in which tungsten atoms are surrounded by 6 oxygens. A decrease in the symmetry of tungsten trioxide leads to the systematic deformation of the WO₆ octahedrons, first stretching and then bending.

Tungsten oxide has attracted a large interest due to its unique applications for example in the transmittance and reflection modulation devices [4,5], and as a photoanode for the use in photoelectrochemical cells [6]. WO₃ is also one of the most widely studied electrochromic [7] and energy storage materials [8]. Moreover, tungsten oxide exhibits properties critical for the fields of bioelectronics and biosensor development [9,10].

An important application of tungsten trioxide is as a sensing layer in gas sensing devices with high sensitivity for both reducing and oxidizing gases [11,12]. Different strategies can be used to enhance

physical properties of tungsten trioxide through its modification: patterning and doping with different elements or compounds where the patterning of the sensing layer increases the active surface [13].

The detection of organic gases is a topic of increasing importance in analytical chemistry, in particular in the context of health monitoring and diagnostics where the composition and concentration of breathed gases is analyzed [14]. One of these gases is acetone which can be used as a diabetes marker. The acetone concentration in breathed gases for a healthy person is lower than for a diabetic patient, typically below and significantly above 1 ppm, respectively, allowing for the distinction between a normal and a high blood sugar level [15–17]. The implementation of the detecting layer onto a flexible substrate for the detection of breathed gases will be another step for improving life quality, for example, in the case of diabetic disease [15,18]. Table 1 reviews the results of acetone gas detection with WO₃ based sensors.

Table 1. Tungsten oxide gas sensing capability for acetone detection.

WO ₃ Based Sensor (Fabrication Method)	Operating Temperature (°C)	Concentration (ppm)	Response (R _{Air} /R _{Gas})	Response/Recovery Time (s)	References
WO ₃ nanostructures (solvothermal)	100	0.05–3.5	~120–700	~500/500	[19]
WO ₃ nanocrystallites with oxygen defects (microwave-assisted hydrothermal method)	320	0.25 100	3.8 31	4/5	[20]
WO ₃ porous nanofibers (electrospinning)	270	0.5–100	~3–60	~10/30	[21]
WO ₃ nanocrystals (sol-gel)	300	0.05–5	~1.2–7.5	>30/>30	[22]
WO ₃ nanotubes (electrospinning)	250	0.5–100	~2.5–45	5/22	[23]
WO ₃ nanolamella/reduced graphene oxide (hydrothermal)	200	1–500	~1.75–30	~2/10	[24]
Fe-C-codoped WO ₃ walnut-like microspheres (hydrothermal)	300	0.2–10	~4.5–17.8	~50/65	[25]
WO ₃ :Si nanoparticles (flame spray pyrolysis reaction)	350	0.1 0.5	1.5 2.75	~10/30 ~10/50	[26]
WO ₃ :Si thin film (reactive DC GLAD 80° sputtering)	425	0.04–3.8	3–40.5	~60/150	[16]
WO ₃ with Ru loaded nanoparticles (acidification + Ru impregnation)	300	0.5–30	~1.5–4 ~6–85 (Ru)	~720/3000	[27]
W ₁₈ O ₄₉ hollow porous spheres with Pt nanoparticles (hydrothermal reaction + atomic layer deposition of Pt)	180	0.5, 20	~1.5, 2.1 ~2.5, 85 (Pt)	13/11 8/26	[28]
W ₁₈ O ₄₉ /α-Fe ₂ O ₃ hollow porous spheres (hydrothermal)	260	0.5–100	~1.6–13.8	10/30	[29]
WO ₃ :C nanoparticles decorating fiber (cotton fiber-template calcination)	300	0.32–5	2–8	3/6–9/12	[30]
WO ₃ :C doped 3D mesoporous (colloidal crystal template)	390	0.9–10	~6–13.5	~60/55	[31]
WO ₃ -SnO ₂ nanorods (hydrothermal and sputtering)	300	100–1000	6–12	3/28	[32]
WO ₃ 3D flower-like nanostructures (hydrothermal)	350	35	22	-	[33]

All aforementioned studies demonstrate the enhancement of detecting capabilities when low dimensional material with a large surface to volume ratio is used. The role of dimensionality is analyzed in recent literature reviews which discuss WO₃ oxides ranging from 0D to 3D nanomaterials and report on the ability of these materials to detect different gasses [12,34]. These reports emphasize the need for future development of the fabrication abilities to produce different hierarchical WO₃

nanomaterials with well-defined structures, high surface areas, and broad internal contact areas to provide more diffusion paths and reactive sites for targeting specific gases.

The improvement of sensing as well electrical, optical, and electrochromic properties of WO₃ films produced with magnetron sputtering can be obtained when a variant of glancing angle deposition (GLAD) technique is used [35,36]. In this approach, a deposition is performed at a non zero incident angle between material flux and normal to the substrate. During GLAD deposition, the film growth begins with the initial nucleation which leads to a random roughness of the film surface. Next, when the deposition continues, a ballistic shadowing and adatoms diffusion effects force a porous growth of columnar structures. Finally, the columns evolve with progressing growth, in particular, the effect of columns broadening and exponential dependence of various morphological parameters (a power law) can be observed. It is well established that the value of incident angle determines porosity and mean density of the film [37], while substrate rotation during GLAD deposition allows for morphology control of columnar growth, reduces anisotropic shadowing effect, and produces columns with more symmetrical cross-section [38]. The rotation rates influence scaling parameters of the growth [39] and when a two-axis substrate rotation is used a zigzag-shaped or helical columnar structures can be formed [40].

The presence of critical angles for various physical properties for GLAD sputtering was described in [41], for example, the critical deposition angle of around 60 degrees for residual stress vs. film thickness was reported. The authors found that these changes are material independent (at least for pure metals), and a result of the deposition method.

When deposited at room temperature the tilted columnar structure is amorphous. Post deposition annealing is needed to induce phase transition [42]. Similar results were reported in [43] where for 500 nm WO₃ nanorod film evaporated at a constant GLAD angle of 70° the triclinic crystallographic structure appeared after annealing at 350 °C.

The positive influence of patterning with GLAD sputtering in gas sensing devices has also been reported. The increase in sensing ability of hydrogen gas by more than an order of magnitude in case of porous nanocolumnar WO₃ film (deposited at the incident angle of 80°) as compared with conventional dense sample was described in [44]. Additionally, a comparison between conventional and GLAD WO₃ thin films (i.e., with the incident angle of particle flux of 0° and 70°, respectively) as an ozone gas was studied in [45]. The authors showed improved detection abilities in GLAD sputtered samples, i.e., higher responses and faster recovery times. These enhancements were attributed to the increase of surface area induced by GLAD deposition process as compared to conventional sputtering. A similar conclusion was found by Xu et al. [46] who studied WO₃ columnar film for dodecane sensing purposes and found the best detecting properties for a sample with highest porous structure. It was shown in [47] that a GLAD sputtered porous WO₃ nanorod thin films can be used for reducing and oxidizing gases, i.e., ethanol and NO₂. The authors concluded that the high surface to volume ratio of porous thin films with nanorod morphology is responsible for the observed good repeatability, as well for high and fast response and sensitivity for both gases. The ability of the tungsten oxide doped with 1% of silicon to sense acetone was studied in [16]. The GLAD angle of 80° and constant rotation speed of the substrate during deposition were used in this study. The response sensitivity above 40 for 3.8 ppm acetone concentration was found at 425 °C while the lowest sensing limit of 0.04 ppm with response of around 4 was found. The authors observed significant increase of sensor response with Si doping.

In this paper, we describe an application of the magnetron GLAD technique to develop sensor surface morphology and to use it to modulate sensor sensitivity.

2. Materials and Methods

2.1. Tungsten Trioxide Deposition

The Magnetron Glancing Angle Deposition technique was employed for the preparation of tungsten oxide thin films. A DC reactive magnetron sputtering from 50 mm tungsten metal target (4.5N,

Kurt J. Lesker Company, Jefferson Hills, PA, USA) was performed in a constant flow of 80% Ar/20% O₂ gas mixture. The gas flow was controlled with a mass flow controller (1179B MKS Instruments, Munich, Germany). The pressure during deposition was 3×10^{-2} mbar, while the initial pressure was lower than 10^{-6} mbar. Using a GLAD manipulator (ECR-UHV-20532-001 from Kurt J. Lesker Company, Jefferson Hills, PA, USA) a series of samples with a different incident angle between 45° and 85° plus 0° were prepared on glass, silicon, and alumina substrates. The deposition was performed simultaneously; samples prepared on glass substrate were then used for ellipsometry spectroscopy, samples prepared on silicon were used for XRR and XRD studies, while gas sensing studies were done using samples prepared on alumina. The samples name notion was set as an angle value with the prefix S, i.e., S0, S45, S70, S75, S80, and S85, giving a total of 6 different samples. Figure 1 presents the sputtering system (a) and a schematic view of GLAD manipulator (b). During the deposition, GLAD α angle was set for a chosen constant degree while the substrate heated to 300 °C was rotated along φ angle at 20 rpm rate. The distance between the target and the substrate was 25 cm. In order to remove any contamination from the target and to ensure stable sputtering conditions a 10 min presputtering process was conducted. After this time a 60 min long sputtering process was performed at a constant power of 50 W. The samples were next annealed at 400 °C in air for 4 h.

Figure 1. Photo of the magnetron sputtering system with a GLAD manipulator (a) and a sketch of the manipulator for GLAD deposition technique (b). Reprinted from [48] under CC BY 4.0.

2.2. XRD/XRR Measurements

The diffraction glancing incident X-ray diffraction (GIXRD) patterns were measured for annealed samples for 3 different omega angle, i.e., 0.5, 1, and 3 degrees using X'PertPro PANalytical diffractometer (Panalytical, Almelo, The Netherlands) with Cu lamp operating at 40 kV and 40 mA. The 2θ angle varied between 20° and 53° with a step of 0.04° and with an accumulation time of 7 s for each step. The data were analyzed with the Rietveld method using FullProf software (version: April 2019) [49]. The X-ray reflectivity (XRR) was performed for omega angle between 0.5° and 2° using the same X'PertPro diffractometer. The XRR analysis was performed with the Parrot method.

2.3. AFM Measurements

The atomic force microscopy (AFM) measurements were performed on the Dimension ICON XR microscope (Bruker, Billerica, MA, USA) at quantitative nanomechanical (uncalibrated) mapping mode which is based on Peak Force Tapping mode. The company's ScanASYST Air blades were used (Bruker, Billerica, MA, USA) with 2 nm nominal blade diameter and constant force lever of 0.4 N/m (silicon blade on silicon nitride lever).

2.4. Spectroscopic Ellipsometry Measurements

Optical measurements, i.e., mean refractive index of thin films and homogeneity maps over sample surface were performed by spectroscopic ellipsometer WOOLLAM 2000 (J.A. WOOLLAM CO., Lincoln, NE, USA) in the range of 200–1700 nm. The maps of homogeneity of thickness and refractive index were measured with light beam collimator with a light beam radius of 130 μm . The movements of the samples were controlled by several XY step motors with 0.1 mm steps.

2.5. Gas-Sensing Measurements

The gas-sensing characterisations were carried out using the gas measurement setup (AGH University of Science and Technology, Krakow, Poland) previously presented in [18,48]. Briefly, the tungsten oxide-based gas sensors were tested under exposure to target gas in the quartz-tube oven. The electrical resistance changes have been measured with a 34401A HP multimeter (Hewlett-Packard, Palo Alto, CA, USA) under exposure to target gas (i.e., acetone) as well as the synthetic air.

Therefore, the gas sensor response (S) was defined as resistance ratio $S = (R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$, where R_{gas} and R_{air} are electrical resistances in gas and air, respectively. The various concentrations of target gas were obtained by the utilization of mass flow controllers and acetone canisters with 5 ppm of acetone (Air Products, Surrey, UK). The gas-sensing measurements were performed at various temperatures and 50% relative humidity (RH) level.

3. Results

3.1. Characterization

3.1.1. XRD/XRR

Figure 2 presents the diffraction patterns gathered for 0.5° omega angle. The green points are data points and the red lines are the fits for a series of WO₃ thin films with different GLAD angles. The results of the other two omega angles, i.e., 1° and 3°, give very similar diffractograms. In order to get diffraction patterns with comparable intensity the signal on the graph was multiplied for sample S85 by 5 and for samples S45 and S0 by 10, respectively. The pattern of sample S0 does not contain any Bragg's maxima but only a wide increase of the signal for small 2 θ angles indicating the amorphous nature of tungsten oxide in this sample. The other samples, i.e., with non zero GLAD tilting angle, show broad diffraction peaks at 2 θ around 24°, 28°, 34°, 42°, 47°, and 50°. A detailed analysis showed that a monoclinic WO₃ phase with $P2_1/c$ space group (ICDD: 01-083-0950) have been formed for all samples (except S0). The observed Bragg's maxima are a convolution of diffraction peaks that emerge from the splitting of specific family planes in monoclinic structure and are marked with blue lines in Figure 2.

The analysis of GIXRD were performed for 3 different omega angles. The mean values of the cell parameters are presented in Figure 3a. The angle β was fixed during analysis with the value of 90.78° taken from the ICDD database. Results for all GIXRD measurements and their mean value are presented in Appendix A (Table A1). In the case of sample S45, because of a weak signal, the a and b cell constants were also fixed at the values found in the ICDD database, and only the c constant was fitted. The strongest changes are found for the b parameter, making it the main reason for observed alterations in cell volume.

In all studied cases (except amorphous S0) a strong crystallographic texture along (002) direction is formed. An analysis, according to the March approach, was performed and the degree of preferred (uniaxial) grains orientation (η) parameter was calculated according to [50]. The mean values of preferred grain orientations, calculated from 3 different omega angle measurements, are presented in Figure 3b. The strongest (002) crystallographic texture above 40% is found for S45 sample while in case of samples deposited with a GLAD tilting angle of 70° or higher a η value is lower by approximately 30%. Interestingly, the η parameters lie around a straight line, showing the influence of GLAD tilting

angle on crystallites growth and their preferential orientation. The higher the tilting angle the weaker (002) crystallographic texture.

Figure 2. Diffraction patterns of WO_3 thin film samples. The green points are data points and red lines are the fits. Blue longitudinal lines show approximated positions of most intensive $\{hkl\}$ family planes. The patterns intensity were multiplied by 10 for samples S0 and S45 while for S85 by 5.

Figure 3. The cell volume V and a , b , c cell constants (presented in the inset) of WO_3 layer (a) and degree of preferred grains orientation along (002) direction (b). The dashed lines on the graph (a) mark the database values of volume and a , b , c constants of the bulk.

Widths of the Braggs maximas were used to obtain the coherence length (L_{coh}) of thin films according to the Scherrer formula (for example see [51]). The coherence lengths, indicating the mean size of crystallites along the direction of the scattering vector, were calculated for the most intensive (002) reflexes. The sizes of XRD crystallites are shown in Figure 4. The values differ for different samples and change between 12 and 28 nm. Figure 4, together with L_{coh} , includes the values of thicknesses of the WO_3 layers determined from XRR analysis (not shown). The data shows that the size of the grains (L_{coh}) is directly connected with the thickness of the WO_3 layer. When the layer is thick the grains are large and, conversely, when the layer is thin the formed grains are small in size.

Figure 4. Thicknesses (black dots) and coherence length (blue dots) of WO₃ thin films.

3.1.2. AFM

The AFM analysis was performed for selected samples. The results are divided into two groups, one for samples S45 and S85, and the other for S70 and S75, and are presented in Figures 5 and 6, respectively. Below the AFM images, three-dimensional visualizations of samples surfaces are presented. The samples S45 and S85 are characterized by relatively flat surfaces with roughness of single nanometers with visible single columns of 5 to 10 nm high randomly scattered on the surface. The number of columns is greater in the sample deposited at a higher tilting angle. The shallow lowering of film level around the columns is found in this sample, presenting the effect of strong shadowing during deposition process with a horizontally rotating substrate.

Figure 5. Atomic force microscopy (AFM) images and corresponding 3D surface visualization of samples S45 (a,c) and S85 (b,d).

Figure 6. AFM images and corresponding 3D surface visualization of samples S70 (a,c) and S75 (b,d).

On the other hand, the morphology of samples deposited at GLAD angle of 70° or 75° is very different. A granular-like surface structure is visible confirming columnar growth of the WO_3 thin film. The observed mean sizes of the structures in those samples (vertical vs. horizontal) are 7.0(3.5) vs. 19.6(4.1) and 13.6(4.9) vs. 24.0(5.5), for S70 and S75, respectively. Standard deviations are given in parentheses. The increase of the size of the individual columns for S75 sample corresponds very well with the maximum of film thicknesses and the value of coherence length found in Figure 4, showing the most effective columnar growth process in this case.

In case of GLAD deposition of tungsten oxide, it was previously observed that an incident GLAD angle larger than 50° leads to clear columnar inclination [52]. The same authors found that the GLAD angle higher than 60° produces well separated columnar structures since the shadowing effect becomes a dominant factor during the deposition process. The results obtained from our AFM analysis are in good agreement with these previous findings. Sample S45 does not show columnar-like growth; instead, surface adatoms diffusion process dominates formation of the polycrystalline thin film. This type of growth leads to the strongest crystallographic texture found for all studied samples. On the other hand, the columnar growth is observed for samples prepared with higher tilting GLAD angles where an increase of the total film thickness is found with a maximum at 75° . For the GLAD angle above this value a reduction of a film thickness is observed as a consequence of a high deposition angle and a large distance between the sputtering target and the sample substrate, leading to less effective columnar growth.

3.1.3. Spectroscopic Ellipsometry

The first step of the spectroscopic ellipsometry study was psi and delta ellipsometric angle measurements in range of 200 up to 1700 nm. A fitting model applied to measured data allowed for the extraction of optical parameters, especially refractive index n and film thickness. Measured data (colored lines) and model (black, dots line) are presented in Figure 7. There were only small differences of refractive indices for thin films deposited in different conditions. The typical wavelength

dependence of refractive index is shown for WO_3 film in Figure 8. The index n increases swiftly for wavelengths below 300 nm, where the maximum is reached, while for the wavelengths above the 300 nm refractive index shows only slight changes.

Figure 7. Ellipsometric angles Psi (red) and Delta (green) together with fitted model (dashed line) for WO_3 thin films measured for different incident angles (55° – 70°).

Figure 8. Refractive index of WO_3 film, thickness 40 nm.

Two types of homogeneity maps were measured. The first one was prepared for thickness of WO_3 films, the second for refractive index. The differences in values of thickness and refractive index were observed only at the edge of the sample where the substrate was fixed to the sample holder. Both types of maps are presented in Figure 9 for S75 sample.

Figure 9. Homogeneity maps of S75 WO_3 film: thickness (a), and refractive index for $\lambda = 632$ nm (b).

3.1.4. Gas-Sensing Characteristics

The gas-sensing characteristics were obtained by utilizing the gas-dosing system previously presented in [48,53]. Briefly, the thin films of WO_3 were deposited on the commercially available gas sensor substrate with interdigital electrodes from BVT Comp., then the sensors were conditioned in the air for 4 h at 400 °C and finally were tested under exposure to acetone and synthetic air. The gas-dosing system is based on the mass flow controllers from MKS Instruments (Munich, Germany), where the gas canisters with initial 5 ppm of acetone in synthetic air (Air Products, Surrey, UK) was used, and various acetone concentrations, i.e., 0.1, 0.25, and 1.25 ppm were prepared with synthetic air (Air Products, Surrey, UK). The concentration range of acetone was selected to fit well with the needs of detecting diabetic disorders. The sensor response was defined as $R_{\text{air}}/R_{\text{acetone}}$, where R_{air} and R_{acetone} are electrical resistances measured under exposure to synthetic air and acetone, respectively. Figure 10 presents the resistance changes as well as the calculated sensor's response for sensors deposited at various angles and tested under the same condition: 300 °C, 50% relative humidity. The sensors were tested under various operating temperatures of 300, 350, and 400 °C as presented in Figure 11a–c, and the map of the obtained results is shown in Figure 11d. The highest responses were obtained for sensors with a gas-sensing layer deposited at 75°. The experiments were repeated several times and the error bars are the standard deviations. Thanks to the glancing angle deposition technique, the films deposited at 75° seem to have a higher surface to volume ratio and, in fact, result in higher sensitivity. However, further confirmation is needed, including cross-sensitivity and long-term stability tests.

Figure 10. Resistance characteristics measured at 300 °C of WO_3 gas sensor for different acetone concentrations and different tilting deposition angle (a) 85°, (b) 80°, (c) 75°, and (d) 70°.

Figure 11. Sensor response for different concentrations of acetone: 1.25 ppm (a), 0.25 ppm (b), and 0.1 ppm (c) and different working temperatures (300 black, 350 blue, and 400 °C green). Representation of the data in the form of maps can be found on the right side of the graph (d).

4. Conclusions

We prepared tungsten oxide thin films from metallic tungsten target using the magnetron Glancing Angle Deposition technique. Our investigation of WO_3 thin films indicates the influence of sputtering geometry on films physical properties, especially sensor properties. We documented the WO_3 phase with different grain size, due to different sputtering angle, by the X-ray diffraction analysis. Thicknesses starting from 12 to 90 nm for different sputtered angles were measured by X-ray reflectometry and we verified samples spatial homogeneity with spectroscopic ellipsometry. The second factor that strongly influenced sensors sensitivity was surface morphology, the property which we measured with AFM. We discovered that films deposited for low (0° , 45°) and high (85°) GLAD angles are more flat than samples deposited at middle tilting angles (i.e., 70° , 75°). We confirmed the granular structure of the surface and columnar growth of the samples prepared at middle tilting angles. The influence of surface roughness on sensors sensitivity was observed by the increase of the sensor response.

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Appendix A

Table A1. The GIXRD results for all measured samples and different omega angles, i.e., 0.5° , 1° , and 3° . a , b , and c parameters are the cell constants. V is a cell volume, η is a degree of preferred grain orientation along (002) direction and L_{coh} is a coherence length.

Sample	Omega (°)	a (Å)	b (Å)	c (Å)	V (Å ³)	η (%)	L_{coh} (nm)
S85	0.5	7.31(3)	7.37(3)	7.687(4)	414.6(22)	28.2(1)	17.5
	1.	7.29(3)	7.40(3)	7.687(5)	415.7(23)	29.0(2)	15.8
	3	7.33(4)	7.40(2)	7.696(6)	417.3(26)	33.2(2)	16.7
	mean	7.31(3)	7.39(3)	7.690(5)	415.8(24)	30.1(2.6)	16.6(9)

Table A1. Cont.

Sample	Omega (°)	a (Å)	b (Å)	c (Å)	V (Å ³)	η (%)	L _{coh} (nm)
S80	0.5	7.32(1)	7.47(1)	7.678(1)	419.9(5)	33.5(3)	25.6
	1.	7.33(1)	7.41(1)	7.690(1)	417.9(6)	34.3(3)	23.7
	3	7.33(1)	7.46(1)	7.609(1)	420.5(7)	35.5(3)	24.5
	mean	7.33(1)	7.45(1)	7.686(1)	419.4(13)	34.4(9)	24.6(9)
S75	0.5	7.32(1)	7.53(1)	7.687(3)	423.9(4)	27.2(3)	28.2
	1.	7.32(1)	7.53(1)	7.690(1)	423.8(2)	27.3(4)	28.6
	3	7.33(1)	7.53(1)	7.696(1)	425.0(2)	29.0(4)	25.9
	mean	7.32(1)	7.53(1)	7.690(2)	424.3(6)	27.9(1.0)	27.5(15)
S70	0.5	7.32(1)	7.51(1)	7.697(1)	422.7(3)	32.9(3)	25.1
	1.	7.32(1)	7.51(1)	7.670(1)	423.5(3)	33.5(3)	24.7
	3	7.32(1)	7.49(1)	7.696(1)	421.9(4)	34.4(4)	23.15
	mean	7.32(1)	7.50(1)	7.697(1)	422.7(8)	33.6(7)	24.3(11)
S45	0.5	7.305	7.535	7.70(1)	423.5(5)		12.2
	1.	7.305	7.535	7.70(1)	423.1(5)		12.7
	3	7.305	7.535	7.71(1)	423.8(7)		11.7
	mean	7.305	7.535	7.70(1)	423.5(6)		12.2(5)
S0	Amorphous	-	-	-	-	-	-

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