

Local Structure of Amorphous Tungsten Oxide Thin Films and Multilayers

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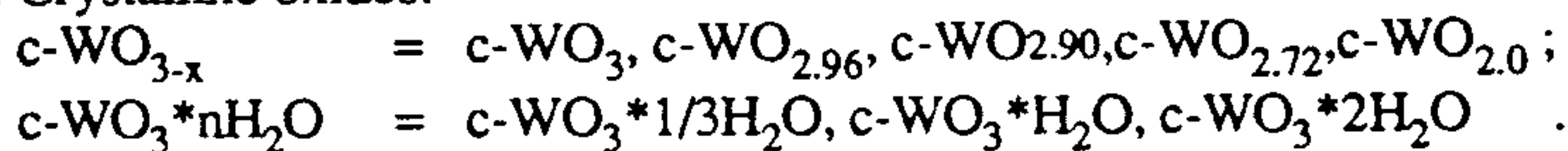
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The EXAFS and XANES spectroscopies have allowed us to investigate multilayer thin film coatings and various multilayer devices due to the selective excitation of a definite type of atom. We have studied a-WO₃ electrochromic multilayer devices on glass (Au/a-SiO₂/a-WO₃/ITO/G) as well as amorphous a-WO₃ thin films evaporated at different substrate temperatures :

a-WO ₃ = a-SiO ₂ /a-WO ₃ /Scotch	- Ts= 50 -350 C
a-WO ₃ = a-WO ₃ /Be	- Ts= 100 C
a-WO ₃ = a-SiO ₂ /a-WO ₃ /Glass	- Ts= 50 -350 C
a-WO ₃ = Au/a-SiO ₂ /a-WO ₃ /ITO/Glass	-Ts= 100 C

The conditions under which tungsten trioxide films are prepared have a remarkable influence upon their electrochromic properties due to the degree of order of the structure, different stoichiometry as well as different contents of water or hydrogen (1). The earlier investigations of the a-WO_{3,0} and tungsten oxides by EXAFS and XANES techniques (2-5) allowed a number of peculiarities in the structure to be established; however, to interpret the peaks with a broad range distribution of bond lengths a more precise description and comparison with crystalline forms of tungsten oxides was necessary.

We have dealt with a number of crystalline oxides to investigate the stoichiometry, the degree of disorder of structure and different contents of water in comparison with a-WO₃ thin films. Crystalline oxides:



EXPERIMENTAL AND RESULTS

Transmission EXAFS and XANES spectra were taken on the W L₃ -edge using the EXAFS station of one the wiggler beam lines (BX-1, "PWA", "ADONE" LNF-INFN). The thin films of a-WO₃ were obtained by thermal evaporation. The thin films, multilayers and crystals were prepared in Inst.Sol.Stat.Phys. - Riga.

The Fourier-transform (FT) of EXAFS spectra $X(k) \cdot k^2$ in the k-space interval 2.5 - 16.0 Å⁻¹ (Fig.1) and the back FT in different R-space intervals allowed us to separate different contributions: 0.8 - 2.2 Å - first coordination shell W-O; 2.2 - 3.2 Å - multiple scattering in first shell W - O; 3.2 - 4.5 - second coordination shell W - O - W with a focusing effects in WO_{3-x} crystals; 4.5 - 6.0 Å - third tungsten coordination shell W - W₂.

Using a multishell theoretical model function (3) in the curve wave approximation to fit the experimental spectra we have obtained a table of structural parameters with $S_0^2=0.5$,

TABLE 1: EXAFS Parameters for the First Coordination Sphere (W-O Pairs)

Compounds	N	R, Å	$\sigma^2, \text{Å}^2$
c-WO _{3.0}	0.6	1.73	0.0001
	1.4	1.76	0.0002
	0.5	1.79	0.0001
	1.5	1.84	0.0005
	1.0	1.91	0.004
	1.0	2.00	0.004
	0.5	2.13	0.004
	1.0	2.16	0.004
c-WO _{2.96}	1.0	1.74	0.0001
	1.0	1.76	0.0015
	1.6	1.78	0.0001
	1.0	1.98	0.0015
c-WO _{2.90}	1.0	1.75	0.0001
	2.4	1.86	0.004
	2.4	1.89	0.005
	1.8	1.97	0.005
c-WO _{2.72}	2.4	1.80	0.0006
	4.8	1.95	0.0025
c-WO _{2.0}	3.0	1.81	0.001
	7.5	1.98	0.0015
	3.0	2.15	0.002
c-WO ₃ *1/3H ₂ O	1.0	1.72	0.0001
	2.0	1.76	0.0001
	2.0	1.86	0.0005
	1.0	2.00	0.0005
c-WO ₃ *H ₂ O	2.3	1.74	0.0001
	2.3	1.87	0.0001
	2.3	1.95	0.006
c-WO ₃ *2H ₂ O	2.0	1.71	0.002
	1.0	1.73	0.001
	2.0	1.86	0.0025
a-WO ₃ /Be	1.2	1.70	0.0005
	3.6	1.75	0.001
	2.4	1.95	0.001
SiO ₂ /a-WO ₃ /Scotch	1.0	1.73	0.0001
	2.0	1.77	0.0003
	2.0	1.88	0.0005
	1.0	2.02	0.001
	1.0	2.20	0.001

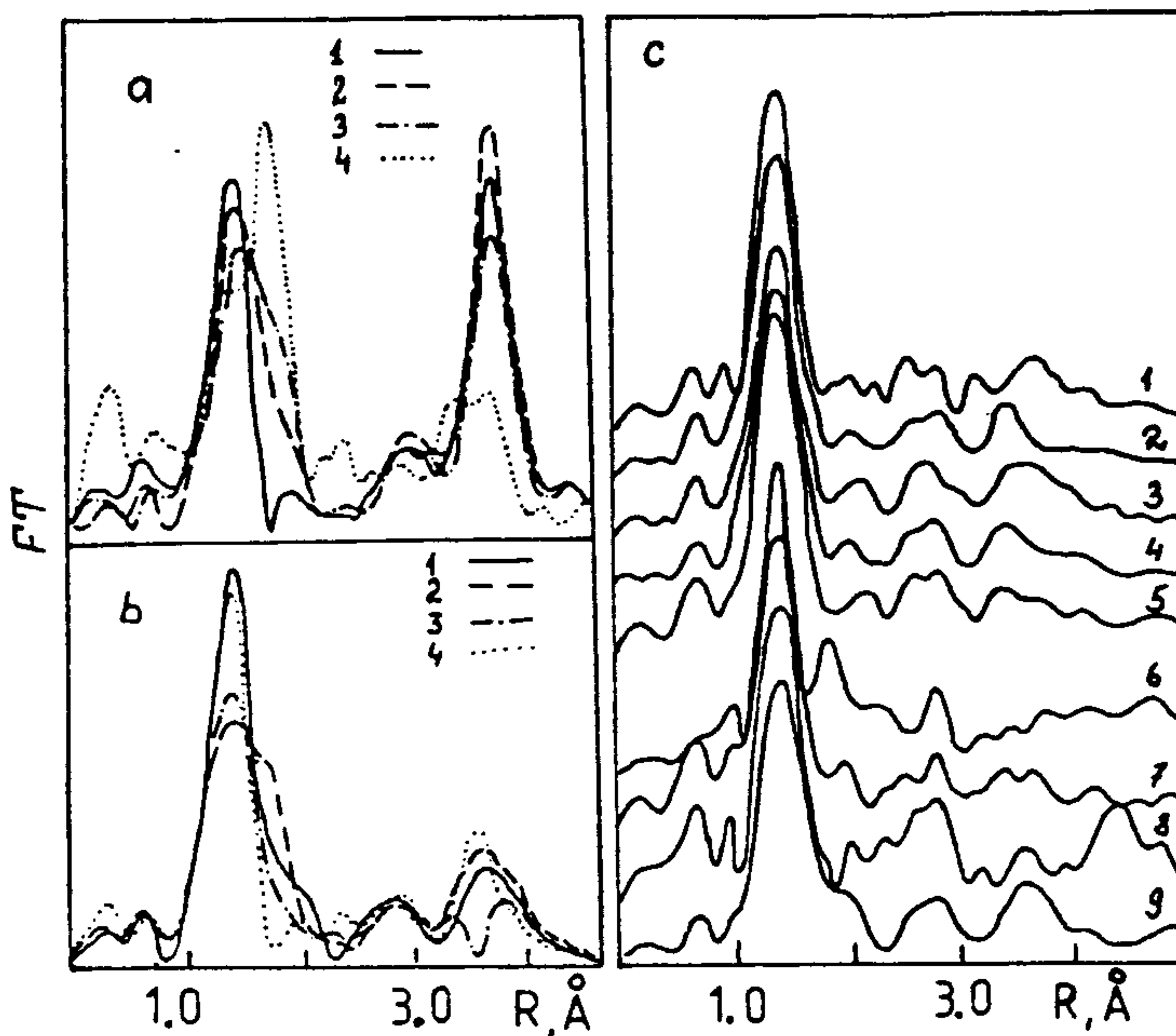


Fig. 1. Fourier transformed EXAFS spectra: c-WO_{2.96} (1a), c-WO_{2.90} (2a), c-WO_{2.72} (3a), c-WO_{2.0} (4a), mon.c-WO_{3.0} (1b), c-WO_{3.0}*H₂O (2b), c-WO_{3.0}*2H₂O (3b), hex.c-WO_{3.0}*1/3H₂O (4b), SiO₂/a-WO_{3.0}/S-50 C (1c), SiO₂/a-WO_{3.0}/S-100 C (2c), SiO₂/a-WO_{3.0}/S-150 C (3c), SiO₂/a-WO_{3.0}/S-200 C (4c), SiO₂/a-WO_{3.0}/S-250 C (5c), Au/SiO₂/a-WO_{3.0}/TTO/Glass (6c), a-WO_{3.0}/Be 100 C (7), SiO₂/a-WO_{3.0}/G (8c), mon.c-WO_{3.0}.

TABLE 2: EXAFS Parameters for the Second Coordination Sphere (W-W Pairs)

Compounds	N	R, Å	$\sigma^2, \text{Å}^2$
c-WO _{3.0}	6.0	3.85	0.008
c-WO _{2.96}	14.0	3.68	0.005
	12.0	3.78	0.002
c-WO _{2.90}	16.0	3.68	0.005
	14.0	3.78	0.002
c-WO _{2.72}	12.0	3.68	0.005
	10.0	3.78	0.002
c-WO _{2.0}	2.5	3.30	0.005
	2.7	3.71	0.003
	3.3	3.85	0.005
a-WO _{3.0} /Be	1.0	3.68	0.006
	1.0	3.80	0.003
SiO ₂ /a-WO ₃ /Scotch	2.0	3.79	0.008
	2.0	3.85	0.008
	2.0	4.00	0.012

$G=0.9$, $E_0 = -4$. A direct comparison of distances shows that the agreement between EXAFS determination (Tables) and crystallographic data is quite good for multishell simulation. The first coordination shell W-O can be divided into three subshells: W = O₁ - terminal oxygens, $R=1.67-1.75 \text{ \AA}$, $\sigma=0.01 \text{ \AA}$; W - O₂ - W - bridging oxygens, $R=1.8-2.0 \text{ \AA}$, $\sigma=0.025 \text{ \AA}$; W---O₃=W - next-nonbridging oxygens (water), $R=2.1-2.3 \text{ \AA}$, $\sigma=0.05 \text{ \AA}$.

The first coordination shell in the a-WO₃ has some similarity with the short range order in hexagonal WO₃*1/3H₂O compound. The structure units were found to be mainly distorted octahedra WO₆ with shared corners. The degree of distortion of WO₆ octahedra increases with apparent hydration (WO₃*nH₂O), the amplitude of the highest peak (W-O) decreases and can be explained by the presence of terminal oxygen in opposite of water O=W---OH₂.

The middle distances of the first coordination shell in the crystals in oneshell fitting in k-space (3.0-10.0 Å⁻¹) are correlate with the valence state of tungsten (W⁶⁺, W⁵⁺, W⁴⁺) and the sum of ionic radii. Therefore in a-WO₃ the valence state is W⁶⁺ and the stoichiometry is close to that of WO_{3.00}.

The peaks in the region 2.2-3.2 Å can be attributed unambiguously to the multiple triple scattering in the first shell (W-O) and probably to terminal and bridging oxygens.

The EXAFS of the second coordination shell (W-W) depends on the bond angle (W-O-W) and for WO_{2.96}, WO_{2.90}, WO_{2.72} crystals can be attributed unambiguously to the focusing effect in c- axis direction. For monoclinic c-WO_{3.0} $R=3.85 \text{ \AA}$, $N=6$, $\sigma^2=0.008 \text{ \AA}^2$ and for c-WO₂ $R=(3.30, 3.71, 3.85) \text{ \AA}$, $N=(2.5, 2.7, 3.3)$ and $\sigma^2=(0.005, 0.003, 0.005) \text{ \AA}^2$ respectively. In the case of a-WO₃ the EXAFS back FT signal is significantly smaller than for the c-WO₃ and the W-W distances have broad range distribution in the range from 3.65 Å to 4.0 Å. The average bond angle (W-O-W) is probably close to 150°.

The XANES spectra (amplitude of white line) differ greatly in each case and depend on the stoichiometry (valence state), different contents of water and degree of disorder of structure. The XANES of a-WO₃ has some similarity with the hydrate crystals WO₃*nH₂O and the white line amplitude is greater than in the crystals.

CONCLUSIONS

Wide energy range and good signal to noise ratio EXAFS measurements allowed us to investigate multilayer thin coatings, electrochromic devices and crystalline compounds with a broad range distribution of bond lengths and different bond angels W - O - W.

The amorphous a-WO₃ thin film consist of corner-sharing distorted and tilted WO₆ octahedra in which the W atoms are off -center .

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