XANES Investigation of the Electronic Structures of Sputter-deposited TiO_2 Nanowires

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Figure 1 compares the Ti $L_{2,3}$-edge XANES spectra of sputter-deposited TiO_2 nanowires obtained at different oxygen contents. The positions of the peaks in the Ti $L_{2,3}$-edge XANES spectra of Fig. 1 (A) are summarized in Table 1. Due to the thickness limitation of our samples, all of the Ti $L_{2,3}$-edge XANES spectra were recorded in the total electron yield mode for Ti 2p absorption. Compared to the fluorescence yield mode, the total electron yield mode is more surface sensitive and therefore better suited when structural information from the surface of the samples is sought. In general, the Ti $L_{2,3}$-edge XANES spectra, characterized by low intrinsic broadening and better energy resolution in comparison to Ti K-edge, provide detailed information about the local Ti bonding configuration and medium-range effects. Therefore, the inspection of the Ti $L_{2,3}$-edge gives complementary data to those obtained from the Ti K pre-edge features about the Ti environment and the particular electronic properties of Ti compounds [1]. As shown in Fig. 1 (A), the Ti $L_{2,3}$-edge XANES spectra for all the samples are split into two sets of peaks between 450 and 472 eV, labeled as L_3 and L_2 edges, separated by ~5.3 eV, due to the spin-orbit coupling of Ti 2p core electrons, which are corresponded to the electronic transitions from the $2p_{3/2}$ (L_3-edge) and $2p_{1/2}$ (L_2-edge) core levels to a 3d excited state of Ti atoms [2]. For both L_3 and L_2 edges, the crystal field splits the 3d state of Ti into t_{2g} (formed by d_{xy}, d_{xz} and d_{yz} orbitals) and e_g (formed by $d_{x^2-y^2}$ and d_{z^2} orbitals) subands in the octahedral symmetry, each L feature reveals two contributions C3 (C2) and D3 (D2), respectively. Moreover, de Groot *et al.* [3] reported that the L_2-edge features are broader than those of L_3-edge originated from a shorter lifetime of the $2p_{1/2}$ core holes due to a radiationless electron transition from the $2p_{3/2}$ to the $2p_{1/2}$ levels, accompanying by the promotion of a valence electron into the conduction band; while an addition or an asymmetry splitting in the e_g peak (E3 and E2) has been attributed to the distortions from octahedral symmetry. The different relative intensity between D3 and E3 peaks indicates different distortions of the local coordination environment, which can be use to distinguish between anatase and rutile TiO_2 polymorphs, i.e. the TiO_2 anatase phase gives of D3>E3, while the TiO_2 rutile phase gives of D3<E3.

We observed that with the increase of oxygen contents from 0% to 100%, the shoulder of e_g band in L_3 edge, i.e. E3 peak, becomes resolved, indicating that the oxygen can give rise to the long-range ordering in the anatase TiO_2 structure. The leading edge of the Ti $L_{2,3}$-edge XANES spectra located between 455.5 and 457.0 eV is shown in Fig. 1 (B). The peak in general shifts to slightly higher absorption energy with the oxygen contents, relative to the sample obtained in pure Ar atmosphere. However, the peak shift behavior makes no difference between O_2=50% and O_2=70%, as well as between O_2=90% and O_2=100%. This result is attributed to the fact that surface oxygen vacancies often associated with ion bombardment during the sputter deposition process, leading to the change of stoichiometric TiO_2 in the near-surface region. V.S. Lusvardi *et al.* [2] demonstrated an investigation of XANES spectra for TiO_2 which exhibited a peak shift with the increase of the oxidation state of titanium. In other words, an L-edge peak of titanium shifts to higher absorption energy and a K-edge peak of oxygen shifts to the lower absorption energy. Y. Kim *et al.* [4] demonstrated that the number of oxygen vacancies can be reduced in the O_2-plasma treated TiO_2 films. In our case, with the increase of oxygen contents, the result leads to increase probability to filling the oxygen vacancies, i.e. increasing the oxidation state of the titanium. Consequently, the surface of the TiO_2 nanowires becomes more stoichiometric with the introduction of oxygen contents, as compared to the sample obtained in pure Ar atmosphere.

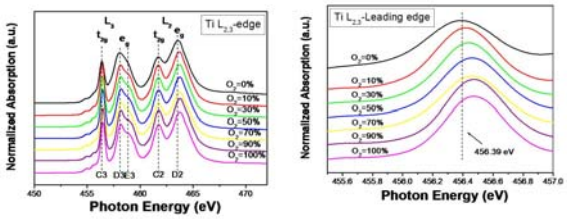

Fig. 1: XANES spectra of (A) Ti $L_{2,3}$-edge, and (B) Ti $L_{2,3}$-leading edge of sputter-deposited TiO_2 nanowires obtained at different oxygen contents.

Table 1: Positions of the peaks in the Ti $L_{2,3}$-edge XANES spectra of Fig. 1 (A). unit:eV

sample	A	B	$\triangle_{BA}$	C	D
O_2=0%	530.77	533.20	2.43	539.14	543.36
O_2=10%	530.66	533.30	2.64	538.99	544.08
O_2=30%	530.72	533.34	2.62	539.12	544.12
O_2=50%	530.71	533.34	2.63	539.10	544.10
O_2=70%	530.71	533.39	2.68	539.15	544.11
O_2=90%	530.66	533.27	2.61	538.97	544.06
O_2=100%	530.70	533.30	2.60	539.10	544.10

$\triangle_{BA}$ represents the energy difference between A and B peaks.