Surface electronic states in three-dimensional SnO$_2$ nanostructures


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(Received 2 March 2005; published 1 July 2005)

The electronic structure of three-dimensional SnO$_2$ nanostructures (aerogels) is studied by soft x-ray absorption near-edge structure (XANES) spectroscopy. High-resolution O $K$-edge and Sn $M_{4,5}$-edge XANES spectra of monolithic nanocrystalline rutile SnO$_2$ aerogels with different surfaces (i.e., different surface-to-volume atom fractions) are compared with spectra of full-density rutile SnO$_2$ and tetragonal SnO. Spectra are interpreted based on the electronic densities of states in SnO$_2$ calculated with both cluster (self-consistent real-space multiple scattering) and band-structure (linear muffin-tin orbital) methods. Results show that, in contrast to the currently widely accepted picture, the presence of undercoordinated surface atoms not only affects the Fermi level position but also changes the structure of the conduction band by introducing additional Sn-related electronic states close to the conduction band minimum. These additional states are due to oxygen deficiency and are attributed to a surface reconstruction of SnO$_2$ nanoparticles forming the aerogel skeleton. Results of this study are important for understanding the physical processes underlying the performance of gas sensors based on SnO$_2$ nanostructures.

DOI: 10.1103/PhysRevB.72.035404 PACS number(s): 71.20.Nr, 71.55.Ht, 78.70.Dm, 82.80.Pv

Tin dioxide (SnO$_2$) is a wide band gap semiconductor with a room-temperature band gap of $\sim$3.6 eV. It is a prototype transparent conductor$^1$ and a model system for metal-oxide-based gas sensors. Doped SnO$_2$ is also used in lithium batteries.$^3$ Additional large interest in this material has recently been stimulated by the demonstration of room-temperature ferromagnetism in SnO$_2$ doped with 3d transition metal impurities$^{4-6}$ and by the fabrication of various quasi-one-dimensional nanostructures, such as nanobelts and nanoribbons.$^7-9$

Most applications of SnO$_2$ are based on its specific surface and/or bulk electronic properties. Numerous previous studies have, therefore, focused on understanding the fundamental electronic structure of bulk and selected low-index surfaces of SnO$_2$ (see, e.g., Refs. 10–23). However, in almost all previous experimental reports,$^{13-16}$ only occupied electronic states (i.e., the valence band region and core levels) have been studied. Hence, a comparison of the experiment and theory has been done for the valence band states only.$^{17-19}$ There are only few previous experimental studies of unoccupied states in bulk SnO$_2$ reporting O $K$-edge x-ray absorption near-edge structure (XANES) spectra (which reflect the O $p$-projected contribution to the conduction band) with qualitative peak assignments.$^{21-23}$ Very recently, Moreno et al.$^{23}$ reported a study of unoccupied electronic states in bulk SnO and SnO$_2$ by electron energy loss spectroscopy focusing on understanding O $K$ edge. However, they$^{23}$ were not able to adequately describe the fine structure of the O $K$ edge of SnO$_2$ with the real-space multiple scattering (RSMS) method.$^{24}$

Tremendous current interest in SnO$_2$ nanostructures has been stimulated by a possibility to develop a new generation of high-performance devices including gas and bio sensors, batteries, and catalysts. However, the fundamental electronic structure of low-dimensional SnO$_2$ remains essentially unexplored. Most of recent numerous reports have focused on the synthesis, structural properties, (UV-visible) optical absorption, and valence band states of SnO$_2$-based nanomaterials.$^{2,7-9,25}$ The structure of the conduction band of SnO$_2$-based nanomaterials, which plays an important role in conductivity and gas sensing mechanisms, has not been investigated.

In this paper, we study the structure of the conduction band in SnO$_2$ aerogels by XANES spectroscopy. Such aerogels are open-cell solid foams derived from highly crosslinked wet gels by drying them under supercritical conditions.$^{26}$ These monolithic foams are characterized by a high degree of porosity ($\geq 90\%$), with ultrafen (nanometer scale) cells/pores. Our results show that, in contrast to the currently widely accepted picture,$^{1,2}$ the presence of undercoordinated surface atoms not only affects the Fermi level position but also changes the structure of the conduction band by introducing additional Sn-related electronic states close to the conduction band minimum. These findings are important for understanding the physical processes underlying the performance of gas sensors based on SnO$_2$ nanostructures.

The SnO$_2$ aerogels were prepared based on an epoxide-initiated gelation method, as described in Ref. 27. The average density of as-synthesized aerogels was $\sim 3\%$ of the full density rutile SnO$_2$. Reference rutile SnO$_2$ and tetragonal SnO powders (with grain sizes $\geq 5 \mu m$) were obtained from Sigma-Aldrich Corp. As-synthesized aerogels were annealed for 1 h in air at temperatures from 250 up to 550 °C. The microstructure of aerogels was studied by x-ray diffraction (XRD, with a CuK$\alpha$ source) and transmission electron microscopy (TEM). The TEM analysis was performed in a Philips CM300FEG microscope operating at 300 kV. Surface area determination and pore volume analysis were performed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using an ASAP 2000 Surface Area Analyzer (Micromeritics Instrument Corp.), as described in Ref. 28.

The XANES experiments were performed at both undulator beamline 8.0 at the Advanced Light Source and...
bending-magnet beamline 8-2 at Stanford Synchrotron Radiation Laboratory. Spectra were obtained by measuring the total electron yield (TEY), by monitoring the total sample photocurrent. The incoming radiation flux was monitored by the total photocurrent produced in a highly transmissive Au mesh inserted into the beam. The overall experimental resolution around O K, Sn M₁, and Sn M₄,₅ edges was ~0.4, ~1.0, and ~0.4 eV, respectively. After a constant background subtraction, all spectra were normalized to the post-edge step heights.

Partial density of states (PDOS) in bulk rutile SnO₂ was calculated with both a cluster self-consistent RSMS method (with the FEFF code, version 8.20)²⁴ and a band-structure linear muffin-tin orbital (LMTO) method.²⁹ In FEFF calculations, clusters of 229 atoms and overlapping muffin tins were used. Both Sn and O potentials were calculated self-consistently within a 5-Å radius, and core holes were fully shielded (i.e., not included in calculations).³⁰ The LMTO calculations were performed in the atomic sphere approximation with six empty spheres in the unit cell. The angular momentum expansions included up to f, d, and p states for the Sn, O, and empty spheres, respectively. Tin 5s, 5p, and 5d states were all treated as valence states, as were the O 2s and 2p states. The valence states were treated semirelativistically, and the core states were recalculated self-consistently using a fully relativistic bound-state solver. The PDOS are not significantly altered when spin-orbit coupling is included in the valence band calculation. The calculations used 168 k points in the irreducible wedge for self-consistency, and a larger grid of 1326 irreducible k points to compute the densities of states in the tetrahedron method. The calculated RSMS and LMTO PDOS were both broadened for a better comparison with experimental data.

The morphology evolution of aerogels during thermal annealing is illustrated in TEM images in Fig. 1. Figure 1(a) shows that the skeleton of the as-prepared aerogel is formed by interconnected particles, ~3–5 nm in size. In addition, XRD, TEM selected-area diffraction (SAD), and high-resolution TEM analyses of both as-prepared and annealed aerogels indicate that the SnO₂ nanoparticles forming the aerogel solid network have the rutile (cassiterite) structure and are randomly oriented. No evidence of the tetragonal (romarchite) SnO phase has been revealed in our aerogels by XRD and SAD analyses.

Figure 1 also shows that annealing at temperatures ≤400 °C has a negligible effect on the average size of nanocrystals. For these annealing conditions, aerogels remain monolithic. However, Fig. 1(d) clearly shows that, during annealing at 550 °C, nanoparticles experience agglomeration and faceting. Such an increase in the nanoparticle size up to ~15 nm [Fig. 1(d)] is also accompanied by a collapse of monolithic samples into powders. This behavior is consistent with previous reports on thermal processing of sol-gel-derived SnO₂ nanomaterials.²

Table I summarizes results of the BET/BJH nitrogen adsorption/desorption analysis for annealed aerogels. It is seen from Table I that thermal annealing at temperatures above ~250 °C results in an expected decrease in surface area and an associated decrease in the average pore volume and an increase in the pore diameter. However, aerogels annealed even at 550 °C still exhibit a relatively high surface area of 55 m² g⁻¹.³¹ These BET/BJH results are consistent with TEM data from Fig. 1. A decrease in the surface area (and, hence, the fraction of undercoordinated surface atoms) with increasing annealing temperature is accompanied by a shrinkage of aerogel monoliths, and, for a temperature of 550 °C, by a collapse of the aerogel superstructure (from a monolithic solid into a powder).

Figure 2 shows XANES spectra over O K and Sn M₄,₅ absorption edges of annealed aerogels. Within the dipole approximation,²² such O K- and Sn M₄,₅-edge spectra reflect electron transitions from the O 1s and Sn 3d (spin-orbit split into 3d₃/₂ and 3d₅/₂ levels, giving rise to M₄ and M₅ edges, respectively) core levels, respectively, into unoccupied electronic states above the Fermi level. If possible core-hole relaxation and electron correlation effects and higher multipole transitions are ignored, such spectra essentially map O-related p-projected (O K edge) and Sn-related p- and f-projected (Sn M₄,₅ edge) states in the conduction band.²³ Figure 2 shows that O K-edge features are broadened for the as-prepared aerogel and become progressively sharper with increasing annealing temperature (and, hence, with decreasing the fraction of surface undercoordinated atoms), approaching the features observed in the spectrum of reference bulk SnO₂.

<table>
<thead>
<tr>
<th>T_{ann} (°C)</th>
<th>SA (m² g⁻¹)</th>
<th>PV (cm³ g⁻¹)</th>
<th>APD (nm)</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>320</td>
<td>1.85</td>
<td>21.5</td>
</tr>
<tr>
<td>250</td>
<td>474</td>
<td>2.97</td>
<td>21.9</td>
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<tr>
<td>400</td>
<td>157</td>
<td>1.44</td>
<td>30.7</td>
</tr>
<tr>
<td>550</td>
<td>55</td>
<td>1.15</td>
<td>48.4</td>
</tr>
</tbody>
</table>

FIG. 1. Bright-field TEM images of SnO₂ aerogels annealed at temperatures of (a) 20, (b) 250, (c) 400, and (d) 550 °C. All four images are of the same magnification.
The low-intensity near-edge features of Sn \( M_{4,5} \) spectra of aerogels are better illustrated in Fig. 3(a), which shows that, with an increase in the surface area, (i) an additional peak centered on \(~4\) eV appears and grows, (ii) the relative intensity of the peak at \(~12\) eV increases, and (iii) all the other peaks exhibit broadening. Such spectral broadening observed in Fig. 3(a) with an increase in the surface atom fraction is consistent with the behavior of O \( K \)-edge features in Fig. 2. Similar broadening has also been observed in several previous XANES studies of other semiconductor nanoparticles (such as InAs, CdSe, and TiO\(_2\)) of similar sizes.\(^3\)\(^4\) In addition, an increase in the intensity of the peak at \(~12\) eV in Fig. 3(a) can be attributed to an overlap of the main peak at this energy from the \( M_5 \) edge and the spin-orbit-split \( M_{4,5} \)-edge counterpart of the additional surface-related feature which is at \(~4\) eV in \( M_{4,5} \)-edge spectra.

To correlate the energy positions of peaks in Sn \( M_{4,5} \)-edge spectra with conduction band features, Figs. 3(b) and 3(c) show Sn \( p \)- and \( f \)-projected PDOS calculated with RSMS and LMTO methods, respectively. In Fig. 3, the major peaks in \( M_5 \)-edge XANES spectra have been aligned with the corresponding features in theoretical PDOS curves, with the conduction band minimum (CBM) at zero energy. It is seen from Figs. 3(b) and 3(c) that relative peak intensities are different in PDOS predictions by these two (also significantly different) theoretical approaches. However, Fig. 3 shows that the energy positions of all three major features in spectra of bulk SnO\(_2\) are well reproduced in the Sn PDOS of \( p \) and \( f \) character, particularly in the case of LMTO calculations. More importantly, such a comparison of theoretical PDOS and experimental XANES spectra shows that the additional (relatively intense) peak at \(~4\) eV, related to under-coordinated surface atoms, lies within the conduction band and not in the band gap.

An insight into the origin of such an additional surface-related peak comes from the fact that spectra of the as-prepared SnO\(_2\) aerogel shown in Figs. 2 and 3(a) are similar to those of bulk tetragonal SnO. This finding is somewhat surprising since, as discussed above, our XRD and SAD analyses have revealed no evidence of the tetragonal SnO...
phase in aerogels. These XANES results are, however, consistent with previous observations that valence-band XPS spectra of bulk SnO$_2$ often resemble those of SnO.\textsuperscript{16} Moreover, recent theoretical studies have predicted that energetically favorable reconstructions of SnO$_2$ (110) and (101) surfaces result in surface O deficiency.\textsuperscript{35} Due to the large surface-to-volume atom fraction in aerogels, such O deficiency, related to the surface reconstruction, is revealed even with a technique (TEY XANES) that probes the entire volume of nanolamigations.

Finally, Fig. 4 shows a series of Sn $M_4$-edge XANES spectra of annealed aerogels [Fig. 4(a)] and corresponding Sn $s$- and $d$-projected PDOS calculated for bulk SnO$_2$ with RSMS [Fig. 4(b)] and LMTO [Fig. 4(c)] methods.\textsuperscript{36} A relatively good correlation between the major features in experimental spectra and PDOS of $d$ character is revealed in Fig. 4. By analogy with the above discussion of Sn $M_4$ spectra (Fig. 3), Fig. 4 further supports the presence of an intense feature (centered on $\sim 4$ eV) related to additional Sn-related surface states. Figure 4 also shows that such additional Sn-related states (apparently, of $s$ character) tail to the CBM, hence, playing an important role in the conductivity and gas sensing mechanisms of potential devices based on SnO$_2$ nanoparticles forming the aerogel solid network.

This work was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48. The ALS is supported by the Director, Office of Science, OBES, Materials Sciences Division, of the U.S. DOE under Contract No. DE-AC03-76SF00098. SSRL is a national user facility operated by Stanford University on behalf of the U.S. DOE, OBES.

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30 Note that FEFF calculations with the core holes included revealed relatively minor changes in the PDOS of SnO$_2$ (such as some changes in relative peak intensities and expected energy shifts) as compared to the ground state PDOS reported in this article.
31 An increase in the effective surface area and pore volume after annealing at 250 °C (see Table I) can be attributed to the desorption of residual organic species from the aerogel surface.
32 See, for example, J. Stöhr, NEXAFS Spectroscopy (Springer, Berlin, 1996).
33 The spin-orbit-split broad, intense features at \( \sim 515 \) and 523 eV in Fig. 2 are due to $3d \rightarrow ef$ transitions. A discussion of such transitions, related to a non-coulombic nature of the potential, can be found in a review by J. P. Connerade, Contemp. Phys. 19, 415 (1978).
36 Compared to the case of Sn $M_{4,5}$-edge spectra (Figs. 2 and 3), in such Sn $M_{4}$-edge spectra in Fig. 4, all features are broadened due to a short lifetime of $3p$ core holes.