Optical Bandgap and Photoconductance of Electrospun Tin Oxide Nanofibers

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Abstract
Optical and photoconductive properties of transparent SnO$_2$ nanofibers, made from C$_{22}$H$_{44}$O$_4$Sn via electrospinning and metallorganic decomposition, were investigated using Fourier transform infrared and ultraviolet (UV)/visible spectrometry and the two-probe method. Their optical bandgap was determined from their UV absorption edge to be 3.95–4.08 eV. Their conductance responds strongly to UV light for a wavelength of 254 nm: in air its steady-state on-to-off ratios are 1.31–1.56 (rise) and 1.25–1.33 (fall); its 90% rise and fall times are 76–96 and 71–111 s, respectively. In a vacuum of about $10^{-4}$ torr, its on-to-off ratios are higher than 35.6 (rise) and 3.4 (fall), respectively, and its 90% rise and fall times are longer than $3\times10^4$ s.

Keywords
fibres, fourier transform spectra, infrared spectra, nanostructured materials, nanotechnology, nanostructurred materials, optical constants, photoconductivity, pyrolysis, semiconductor growth, semiconductor materials, tin compounds, ultraviolet spectra, visible spectra

Comments
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Optical and photoconductive properties of transparent SnO2 nanofibers, made from C22H44O4Sn via electrospinning and metallocrnic decomposition, were investigated using Fourier transform infrared and ultraviolet (UV)/visible spectrometry and the two-probe method. Their optical bandgap was determined from their UV absorption edge to be 3.95–4.08 eV. Their conductance responds strongly to UV light for a wavelength of 254 nm: in air its steady-state on-to-off ratios are 1.31–1.56 (rise) and 1.25–1.33 (fall); its 90% rise and fall times are 76–96 and 71–111 s, respectively. In a vacuum of about 10−4 torr, its on-to-off ratios are higher than 35.6 (rise) and 3.4 (fall), respectively, and its 90% rise and fall times are longer than 3 × 104 s. © 2007 American Institute of Physics. [DOI: 10.1063/1.2800261]

INTRODUCTION

Transparent conductive oxides (TCOs) have received extensive attention because of their important optoelectronic applications such as electrochromic devices, transparent electrodes, and antireflection coatings in solar cells. Tin oxide or stannic oxide (SnO2) is a typical TCO with a tetragonal rutile structure and a bandgap (Eg) of around 3.6 eV, which makes it transparent to light up to the ultraviolet (UV). It is also chemically inert, mechanically hard, and thermally heat resistant and has seen additional applications as sensors, heat mirrors, and heterogeneous catalysts. Its conductivity can be changed drastically either by extrinsic impurity doping or by intrinsic formation of oxygen vacancies in its lattice, which donate electrons. Since film is the preferred morphology for most optoelectronic, sensing, and heat reflecting applications, SnO2 films have been synthesized by numerous methods, such as chemical vapor deposition, sol-gel, spray pyrolysis, and polymeric precursor. However, for many applications such as the line light source or dielectric waveguide, the fiber morphology is more favorable. Unfortunately, so far only a few ways, such as thermal decomposition, template and oxidation, laser ablation or vapor-liquid-solid growth, vapor deposition, and electrospinning, have been developed to fabricate SnO2 nanofibers or ribbons. Their optical and optoelectronic properties have been barely touched even though such property characterization is indispensable for their optoelectronic applications. For example, only Liu et al., Lee et al., and Mathur et al. have evaluated the photoconductance of SnO2 nanowires and only Lee et al. have presented their UV photoresponse. To our knowledge, no report has been made neither on the optical bandgap (Eg) of SnO2 nanowires, an important parameter for their optoelectronic applications in general, nor on the photoconductance of electrospun SnO2 nanofibers. We have developed two recipes for electrospinning SnO2 fibers, characterized their electrical properties, and applied a single electrospun SnO2 fiber in gas detection. This letter investigates their optical and photoconductive properties, with its emphasis on the determination of their optical bandgap and evaluation of their conductive response to UV light.

EXPERIMENT

The synthetic procedure and characterization methods for SnO2 fibers have been reported in details. Briefly, precursor fibers and mats were electrospun from a solution of commercial poly(ethylene oxide) (molecular weight of 900 000), chloroform, and dimethyldi(ethylene oxide) tin (C22H44O4Sn) using a homemade electrospinning setup onto quartz plates, for subsequent spectral characterization, and (111)-oriented single crystal silicon wafers with their surface thermally oxidized and patterned with gold contacts, for subsequent conductive measurement. The as-deposited precursor fibers and mats were subsequently thermally decomposed in air for 2 h at 100, 200, 300, 400, 500, and 600 °C, respectively. Our previous x-ray diffraction, Raman microspectrometry, and Fourier transform infrared (FTIR) spectrometry characterization indicated that the fibers are rutile-structured SnO2 after thermal decomposition at and
FIG. 1. (Color) (a) FTIR and (b) UV/VIS spectra of as-deposited and thermally decomposed fibers. [The inset in (a) shows the disappearance of the C–H stretching band].

FIG. 2. Determination of optical band-gap ($E_g$) from the UV absorption edge. (Solid and dashed curves are experimental and linear fitting/extrapolating, respectively.)

FIG. 3. (Color) Transient UV responses in air: (a) $G$ vs $t$ (time) and (b) $\Delta G$ vs $\Delta t$. 
above 400 °C.\textsuperscript{15,16} Optical properties of mats decomposed at different temperatures were measured using a Perkin-Elmer Spectrum One FTIR spectrometer and a Perkin-Elmer Lambda 35 ultraviolet/visible (UV/VIS) spectrometer. Mats samples were directly used for the UV/VIS analysis. For the FTIR analysis, mats were mechanically stripped off their substrate as powder which was sampled using the Nujol-mulling technique.\textsuperscript{16} Electrical measurement was conducted on a single fiber decomposed at 600 °C using the two-probe method in air and in a vacuum about 10^{-4} torr. The UV light source is a Minerallight UVGL-25 lamp with its maximum output power density of 460 μW/cm^2 at the wavelength (λ) of 254 nm.

RESULTS AND DISCUSSIONS

FTIR spectra [Fig. 1(a)] reveal that organic groups in precursor fibers decompose mostly between 200 and 300 °C and the fibers transform into incipient polycrystalline rutile structure at around 400 °C.\textsuperscript{16} The synthesized fibers demonstrate a strong absorption band around 600 cm\textsuperscript{-1}, characteristic of the stretching Sn–O vibration of transverse Eu mode in the rutile-structured SnO\textsubscript{2}.\textsuperscript{19,20} On the other hand, the fibers are transparent from near IR (λ=1100 nm) to their UV absorption edge. The edge shifts toward the longer wavelength when the thermal decomposition temperature (TDT) increases from 100 to 300 °C, above which further shift is not evident [Fig. 1(b)].

It is well accepted that the bandgap is direct in the rutile-structured SnO\textsubscript{2}.\textsuperscript{1–3} During its direct interband transition, the optical absorption coefficient α follows as a function of incident photon energy (E) on the long-wavelength (low E) side,

\[ \alpha = [A(E - E_o)]^{1/2}, \quad (1a) \]

or

\[ \alpha^2 = A(E - E_o), \quad (1b) \]

where \( E_o \) is the optical bandgap and \( A \) is a constant.\textsuperscript{21} Since \( \alpha \) and transmittance (T) are correlated as

\[ T = e^{-\alpha L}, \quad (2a) \]

or

\[ \alpha = -\frac{\ln T}{L}, \quad (2b) \]

where \( L \) is the thickness of the sample, we have

<table>
<thead>
<tr>
<th>TDT (°C)</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_o ) (eV)\textsuperscript{a}</td>
<td>3.985±0.004</td>
<td>3.997±0.001</td>
<td>3.952±0.002</td>
<td>4.087±0.002</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The errors given in this report are fitting errors.

\[ (\ln T)^2 = AL^2(E - E_o), \quad (3) \]

which predicts a linear relation between (\( \ln T \))^2 and E. Such a linear relation is confirmed in the photon energy range of 4.3–5.2 eV (Fig. 2), and its extrapolation to the \( E \)-axis gives us \( E_o \) values for different TDTs (Table I). Overall, the \( E_o \) value increases with heat treatment temperature (HTT) but the variation is very small. The values lie within the reported range of 3.8–4.2 eV for SnO\textsubscript{2} thin film determined in the same way\textsuperscript{5–7} and are higher than \( E_g \approx 3.6 \text{ eV} \). The difference may be attributed to the Burnstein-Moss effect\textsuperscript{22,23} (due to the filling of the conduction band by free carriers\textsuperscript{24}), the two-dimensional quantum confinement (quantum wire) effect caused by the porosity,\textsuperscript{25} as well as the defect effect.\textsuperscript{5} In literature (Ref. 26, for example), \( \alpha^2 (i=1/2, 1) \) and \( (\alpha E)^j (j =1/2, 1, \text{and } 2) \) against \( E \) have also been linearly fitted and extrapolated to determine \( E_o \) values. Such processing sometimes results in approximately the same \( E_o \) values as listed in Table I or values closer to the \( E_g \) value. However, they are based on assumptions that cannot be justified for rutile-structured SnO\textsubscript{2} (for example, an indirect bandgap) (Ref. 27) and are not adopted here.

The fiber’s conductance (G) is insensitive to visible light, which is consistent with its transparency to visible light [Fig. 1(b)]. However, G is sensitive to UV light of 254 nm wavelength (Figs. 3 and 4). Upon the UV illumination in air, G increases sharply and then asymptotically to its steady value with the on-to-off ratio (\( \xi \)) of 1.58 (first cycle) and 1.31 (second cycle); when the UV light is turned off, G decreases asymptotically to its new steady values with \( \xi =1.33 \) (first cycle) and 1.25 (second cycle). The 90% rise and fall times \( (t_r \text{ and } t_f) \) of the conductance are 111 and 96 s (first cycle) and 76 and 71 s (second cycle), respectively. It is also interesting that G changed by 19.6% after the first UV on-and-off cycle, implying an only partially irreversible change. However, its change is only 3.5% in the second cycle. In fact, the G change follows

\[ TDT vs \xi \]

\[ \Delta t vs \Delta t \]

Fig. 4. (Color online) Transient UV responses in vacuum of ~10^{-4} torr: (a) G vs time and (b) \( \Delta \sigma \) vs \( \Delta t \).
TABLE II. Main photoresponsive characteristics of the fiber.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Cycle</th>
<th>$\xi$</th>
<th>$t_r$, or $t_f$ (s)</th>
<th>$\Delta G_0$ ($\mu$S)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In air</td>
<td>First rise</td>
<td>1.56</td>
<td>$t_r=96$</td>
<td>2.349±0.009</td>
<td>36.1±0.5</td>
</tr>
<tr>
<td></td>
<td>First fall</td>
<td>1.33</td>
<td>$t_f=111$</td>
<td>1.533±0.006</td>
<td>23.1±0.5</td>
</tr>
<tr>
<td></td>
<td>Second rise</td>
<td>1.31</td>
<td>$t_r=76$</td>
<td>1.543±0.005</td>
<td>23.7±0.4</td>
</tr>
<tr>
<td></td>
<td>Second fall</td>
<td>1.25</td>
<td>$t_f=71$</td>
<td>1.304±0.003</td>
<td>18.5±0.3</td>
</tr>
<tr>
<td>In vacuum</td>
<td>Rise</td>
<td>&gt;35.6</td>
<td>$t_r&gt;30432$</td>
<td>4.384±0.002</td>
<td>852±15</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>&gt;3.40</td>
<td>$t_f&gt;30910$</td>
<td>3.536±0.001</td>
<td>11227±11</td>
</tr>
</tbody>
</table>

$\Delta G = \Delta G_0(1 - e^{-\Delta G/\xi})$,  

where $\Delta t$ is the time measured from the UV-switching moment and $\Delta G_0$ and $\tau$ are listed in Table II. While $\Delta G_0$ is proportional to $\xi$, $\tau$ is also a measure of response time, corresponding to $\Delta G$ change by 63.8% and less than $t_r$ and $t_f$ (Table II). The wide optical bandgap and high photoconductivity imply promising optoelectronic applications of the nanofibers. It is noteworthy that the photoresponse times and gas-sensing response times are close, both characteristic of the surface adsorption and desorption processes triggered by switching of either analyte or UV light. In vacuum the evacuation of the reducing moisture from the chamber and therefore adsorbed $O_2^−$ species on the SnO$_2$ surface. The adsorption and desorption processes discussed in the previous paragraph still work, only with a lower partial pressure of oxygen ($P_{O_2}$), a lower surface concentration of $O_2^−$ ($[O_2−]$), and accordingly, a thinner depletion layer than in air. The thinner depletion layer can be totally eliminated by the UV illumination and G will be increased more in vacuum than in air. Kinetically, however, the lower $P_{O_2}$ and $[O_2−]$ values slow down reactions (4) and (5) in vacuum, resulting in longer photoresponse times than in air.

**CONCLUSIONS**

Optical and photoconductive properties of electrospun tin oxide nanofibers were investigated in UV, VIS, and IR ranges. It was found that the fibers are transparent from 1100 nm to their UV absorption edge. Their optical bandgap lies between 3.95 and 4.08 eV. In air, the conductance of a fiber heat treated at 600 °C responds sensitively to UV light of 254 nm wavelength (4.89 eV photon energy), with its steady on-to-off ratios 1.31–1.56 (rise) and 1.25–1.33 (fall) and its 90% rise and fall times between 76–96 and 71–111 s, respectively. The photoresponse in vacuum is stronger and slower, with the on-to-off ratios higher than 35.6 (rise) and 3.4 (fall), respectively, and the 90% rise and fall response times longer than $3 \times 10^5$ s.

**ACKNOWLEDGMENTS**

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