Hydrogen as a Potential Cause for Native n-type Conductivity in Tin Dioxide

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Abstract:

Tin dioxide (SnO_2) has been widely used for chemical sensors and transparent conductive films because of its wide band gap energy of 3.6 eV and n-type conductivity. The exact cause of this native n-type conductivity is not well-known, but density functional theory (DFT) calculations suggest that hydrogen (H) act as "hidden" shallow donors in SnO_2 [1]. To overcome the difficulty of analyzing hydrogen-related phenomena, this analytical study was performed using ^2H as an isotopic tracer. Pure and In-doped SnO_2 ceramics were annealed in humid O_2 gas enriched with ^2H_2O to introduce ^2H into the SnO_2 lattice. Characterization was performed with thermal desorption spectroscopy (TDS) and secondary ion mass spectroscopy (SIMS), as well as Raman, photoluminescence (PL) and Fourier transform infrared (FTIR) spectroscopies. Results indicate that the hydrogen that compensates the acceptor states created by indium, thus preventing p-type conductivity, mostly sit in defect sites that are more stable than those of the hydrogen that was introduced through the humid annealing process. The more stable defect sites are thought to be substitutional sites, while the less stable defects are thought to be interstitial sites.

Introduction:

The native n-type conductivity of SnO_2 is often explained by assuming that oxygen vacancies act as shallow donors, but recent density functional theory calculations claim that oxygen vacancies are too deep to act as shallow donors and instead point to hydrogen as acting as "hidden" shallow donors in SnO_2 [1]. These calculations also indicate that indium and gallium could create shallow acceptor states in SnO_2 that would cause p-type conductivity [1]. However, p-type tin dioxide has never been obtained experimentally. DFT claims this is because the acceptor states created by gallium and indium are compensated by hydrogen [1].

The technique of using isotopic tracers allows characterization based on the mass difference between isotopes. Ideally, a common isotope is exchanged for a less common isotope — ^2H for ^1H in this case. The ^2H is introduced to the system via ^2H_2O. This ^2H_2O then becomes $^2H^1HO$ through an exchange process that allows ^1H to be replaced by ^2H. The ^1H that was previously in the lattice is then carried off by $^2H^1HO$, while the ^2H diffuses further into the lattice.

Experimental Procedure:

Pure and In-doped SnO_2 bulk ceramics were used in this study. Before beginning the humid annealing process, they were polished and sintered to smooth the surface and repair mechanical damage. To introduce ^2H into the SnO_2 lattice as an isotopic tracer, samples were annealed in humid O_2 gas enriched with ^2H_2O for one hour at 200°C, 300°C or 400°C. The ^2H_2O contained 98 atomic% ^2H and had a dew point of 60°C, resulting in an absolute humidity concentration of about 19.6 volume%.

Samples were characterized before and after annealing, mainly using methods that took advantage of the difference in mass between ^1H and ^2H. These methods include TDS, in which the samples are heated from room temperature to 1000°C to create a desorption profile for reactivity analysis; and SIMS, in which the material surface is sputtered to create a composition depth profile for diffusivity analysis. Other characterization techniques used include PL, Raman and FTIR spectroscopes.

Results and Conclusions:

TDS was used to analyze defect stability because it gives information about how much energy is needed to desorb a certain species. Thus, the higher the desorption temperature, the greater the stability of the species. This can be translated to the stability of a species in a particular defect when the species are isotopes, so the main difference between the two is their
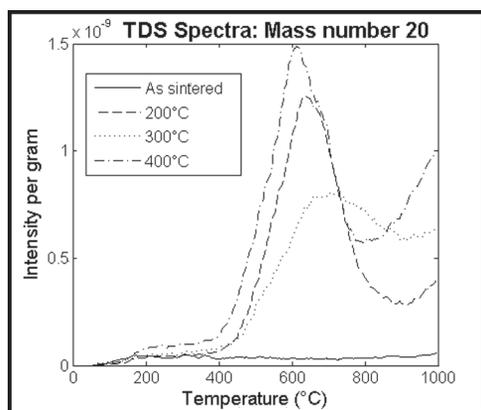
Figure 1: TDS spectra of In-doped SnO_2 for mass number 20, which corresponds to ^2H_2O.
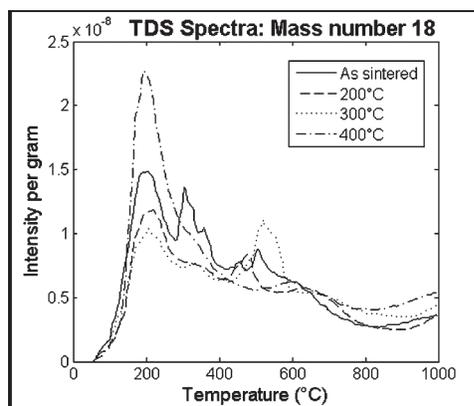
Figure 2: TDS spectra of In-doped SnO_2 for mass number 18, which corresponds to ^1H_2O.
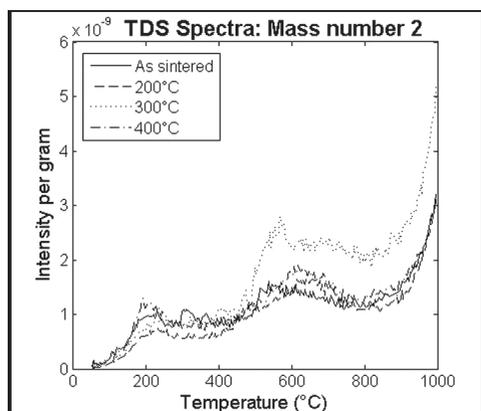
Figure 3: TDS spectra of In-doped SnO_2 for mass number 2, which corresponds to $^1H_2$.
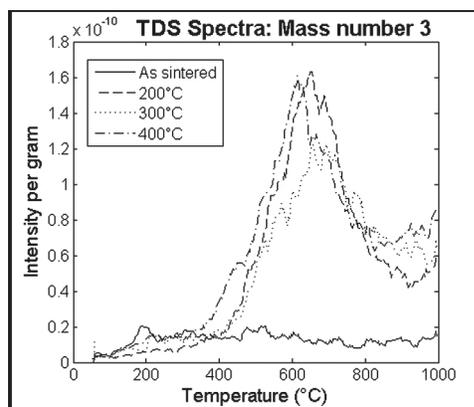
Figure 4: TDS spectra of In-doped SnO_2 for mass number 3, which corresponds to $^1H^2H$.

surroundings. Peaks at 610-690°C and around 1000°C were deemed to be the most important for understanding hydrogen behavior. In the ranges of interest, mass number 2 corresponds to $^1H_2$, mass number 3 to ^1H_2H, mass number 18 to ^1H_2O, and mass number 20 to ^2H_2O.

For mass number 20 (Figure 1), there was a strong peak at 610-690°C for the annealed samples, but no peak for the sample that had not been annealed, as expected. However, there was no peak in that same range for mass number 18 (Figure 2), which indicates that hydrogen was likely being added to SnO_2 lattice instead of being exchanged. This was supported with SIMS data that showed the concentration of ^2H in the In-doped ceramics was approximately an order of magnitude higher than that of the pure ceramics.

For mass number 2 (Figure 3), the dominant hydrogen peak was around 1000°C, while the dominant hydrogen peak for mass number 3 (Figure 4) was at 610-690°C for the annealed samples. This indicates that the ^1H that was initially in the In-doped ceramics and compensated the acceptor states created by In mostly sat in stable defect sites. The ^2H that was added to the material sat in less stable defect sites. These sites are believed to be substitution and interstitial sites, respectively, because of their relative stabilities.

Acknowledgments:

References:

[1]   Singh, A., et al.; "Sources of Electrical Conductivity in SnO_2"; Physical Review Letters, 101.5, 055502 (2008).