

Hydrogen Impurities in Tin Dioxide Films Deposited by Pulsed Laser Deposition

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Abstract and Introduction:

Tin dioxide (SnO₂) is well known for its use as a gas sensor and transparent conducting oxide. It has a rutile-type crystal structure, room temperature band gap of 3.6 eV, and it is a native n-type semiconductor. The source of its n-type conductivity is not well known. Typically, the source is assumed to be oxygen vacancies. As shown in Figure 1, the removal of an oxygen ion causes a charge imbalance, and, to return to charge neutrality, electrons are injected into the material. However, recent density functional theory (DFT) calculations have shown that these oxygen vacancies are actually deep-level donors that are about 1 eV below the conduction band [1]. The electrons contributed by these vacancies are too deep to be activated at room temperature by thermal energy. Therefore, it is unlikely these oxygen vacancies are the source of the native n-type conductivity.

However, DFT calculations also predict that hydrogen acts as a shallow donor in SnO₂ [1, 2]. Hydrogen (H) impurities can inject electrons by nesting H atoms at interstitials in the crystal lattice, directly adding an electron to compensate the addition of a positively charged impurity, or the atoms can replace oxygen atoms within the crystal lattice as hydride ions. The replacement results in electron injection, as seen in Figure 1.

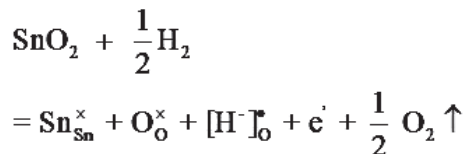
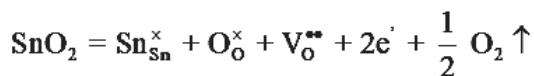


Figure 1: Chemical equations showing the production of electrons due to either oxygen vacancies (top) or hydrogen impurities (bottom).

It is clear that understanding the role and effects of H within SnO₂ is very important. As such, the goal of this project was to deposit samples with plasma laser deposition (PLD) and correlate their H concentration with other physical properties. By using PLD, it was possible to ensure the SnO₂ composition and control the thickness, surface morphology, and homogeneity of the resulting films.

Experimental Procedure:

Initially, fused silica substrates were prepped, loaded into the main PLD chamber, heated to 500°C, and held at that temperature for 40 minutes during which deposition took place. As shown in Figure 1, during deposition a SnO₂ ceramic pellet of purity greater than 99.99% was contained within a chamber with a background oxygen partial pressure of 1.4 × 10⁻⁵ Torr and an oxygen radical gun aimed at the substrate. Then, a laser ablated the surface of the target, creating a plasma that deposited SnO₂ onto the substrate.

After deposition, the sample thickness was measured in a Dektak contact profilometer, the surface morphology was characterized with dynamic force microscopy (DFM), the defect states were determined with photoluminescence (PL), and the crystal structure was checked with x-ray diffraction (XRD) to ensure SnO₂ was deposited. Then, aluminum electrodes were evaporated onto the sample and its Hall effect was measured. Finally, secondary ion mass spectrometry (SIMS) measurements of the samples were taken to observe the concentration of H within the samples.

Results and Conclusions:

After compiling, plotting, and comparing characterization results, it became clear that samples' H concentrations were very sensitive to changes in deposition conditions. A sample deposited after many runs had an order of magnitude lower H contained than did one deposited right after opening the chamber. Comparing these results to the corresponding Hall

effect data, Figure 2 shows that the carrier concentration cannot be correlated to the H concentration in these samples. As H was expected to be the source of the carriers, this was quite unexpected. Further, from Figure 2 it was clear that large amounts of H were already introduced into the samples during deposition.

These two observations call into question whether or not H is actually acting as a shallow donor. Were the sample to have no defects, the H atoms would be incorporated into the crystal lattice as interstitials — thereby injecting electrons and acting as a shallow donor. However, if there are some defects, such as deep acceptors, the acceptor, which is usually tied to a positive hole, will preferentially bond to any introduced H instead and the electron that would have been injected with this addition of H will be compensated by the hole that was originally tied to the acceptor.

Therefore, all deep acceptors would need to be compensated before H could begin to provide more charge carriers. As it is, PL measurements, represented in Figure 3, indicate three different defect states that luminesce in the visible light range.

Clearly, hydrogen does not seem to affect SnO₂ as expected. Further studies must be done to better understand the role of hydrogen, if there is one.

Future Work:

In order to see if additional hydrogen might better illuminate hydrogen's effects on the tin dioxide's physical properties, annealing studies were also performed. These studies are still ongoing at the National Institute for Materials Science (NIMS), and the results obtained for the annealed samples will be published elsewhere by NIMS researchers.

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References:

- [1] Singh, Abhishek Kumar et al., "Sources of Electrical Conductivity in SnO₂"; Physical Review Letters, 101 055502, Aug. 2008.
- [2] Hlaing Oo, W. M. et al., "Hydrogen donors in SnO₂ studied by infrared spectroscopy and first-principles calculations"; Physical Review, B Volume 82 193201, Nov. 2010.

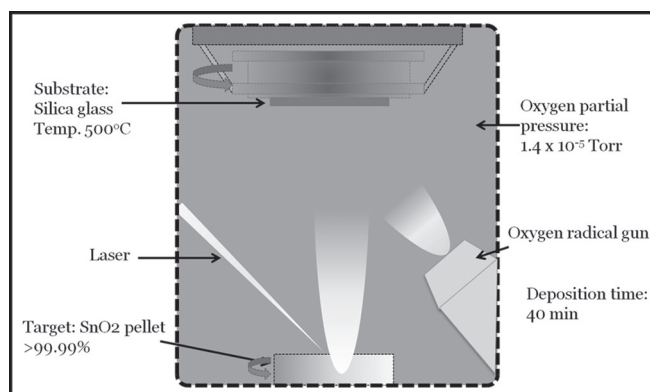


Figure 2: Schematic of how the PLD operates.

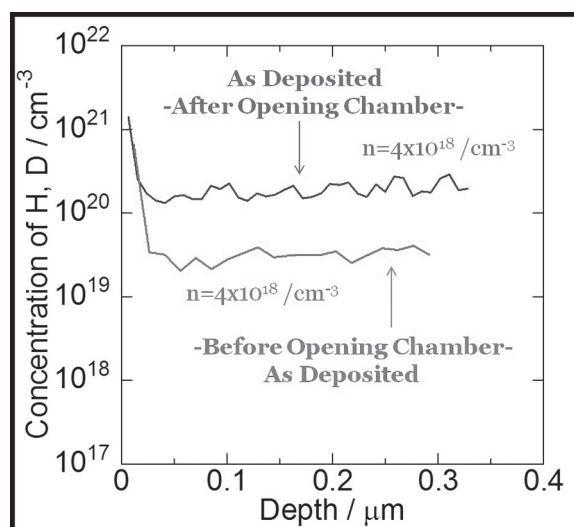


Figure 3: Plot of SIMS data showing, for two different samples, the concentration of hydrogen and deuterium as a function of depth.

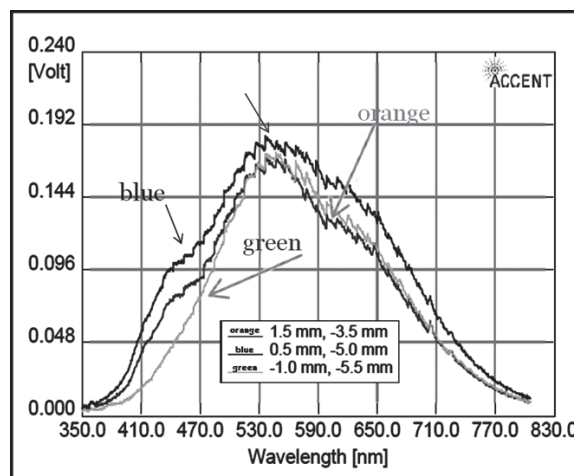


Figure 4: Plot of PL data indicating the presence of defects causing luminescence in the visible light range.