Investigating the Optical Properties of Tungsten Oxide Thin Films for Selective Hydrogen Gas and Sodium-Ion Sensing

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by

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Abstract

Tungsten oxide is a prominent n-type transition metal oxide with unique electrical and optical properties. Due to its excellent chromic properties, it has been extensively studied for developing electrochromic devices, gasochromic sensors, photocatalysts, etc. Recent years have seen a lot of research on tungsten oxide-based gasochromic Hydrogen sensors due to their simple construction and low thermal energy requirements. This thesis investigates the optical properties of tungsten oxide for a) low-temperature gasochromic Hydrogen sensing and b) Sodium ion detection from aqueous solutions. Sol-gel spin coating and electrochemical deposition methods are discussed in the context of WO_3 thin film synthesis under different preparation conditions.

For optical H_2 gas sensing, gasochromic Pt/Pd doped WO_3 films are prepared under different sol concentrations and metal doping concentrations. UV-VIS-NIR spectroscopy of the samples is recorded for the samples by alternatively purging 4% Hydrogen gas (in nitrogen balance) and synthetic air (80% N_2+20% O_2). Dynamic transmittance changes are measured for the Pt/Pd-WO_3 samples at low operating temperatures below 100°C at 650nm. The sample giving optimum response is further inspected for low-concentration detection of H_2. 2wt% Pt doped film prepared from PTA sol of moderation concentration gave greater transmittance changes at 70°C and response recovery times within 40s. The sensor can detect H_2 concentrations down to 0.01%. Detailed material characterization of the samples was done to study the effect of material structure and doping on the optical sensing results. W 4f spectra of the samples revealed that the prepared samples were stochiometric. Analysis of Pt4f and Pd3d spectra showed that PtO: Pt contributed to the higher catalytic activity towards Hydrogen dissociation as compared to PdO: Pd and hence better sensing in the case of Pt-doped samples. Raman spectroscopy confirmed the monoclinic structure of the WO_3 and the presence of W=O due to hydrous phases. With several cycles of H_2 and Synthetic air purge, water accumulates on the tungsten oxide surface and blocks the reaction sites. Increasing the operating temperature to 100°C led to the elimination of water and enhanced the gasochromic properties. This study can be further extended for optical methane sensing by using the photocatalytic properties of tungsten oxide.

As a second part of the work, electrodeposited WO_3 films are used for selective Sodium ion detection, which finds applications in food industries and clinical diagnosis. Transmittance changes are observed for samples in different NaCl concentrations in 0.1M TRIS

buffer and DI water. The results show that transmittance increases with NaCl concentration at a particular wavelength range due to Na^+ ion diffusion. ΔT_{max} calculated as the difference in transmittance measured 10 minutes after insertion in NaCl and immediately after insertion in NaCl solution showed a linear response with respect to concentration at ~300 nm. Also, the sample showed better selectivity towards Na^+ than other alkali ions such as K^+ and Ca^{2+}. FESEM images of the films depicted the porous structure with cracks that facilitate higher ion insertion. W4f spectra of the samples before insertion in NaCl solution showed the presence of W^{6+} and W^{5+} states. These W^{5+} color centers are formed during cathodic deposition and did not oxidize after annealing at 300°C. The Na1s spectra of the samples taken after insertion in NaCl solution had a higher intensity and peak area, confirming the diffusion of Na^+ ions. An analysis of the Raman spectra of the electrodeposited samples revealed a monoclinic crystal structure and the presence of initial absorbed water on the film's surface (W=O).

Scope of the present work

To investigate the optical properties of tungsten oxide for low-concentration detection of Hydrogen gas at safe operating temperatures. To study tungsten oxide's Na^+ ion sensing properties using a simple method based on measuring the transmittance changes at a particular wavelength range.

Objectives of the present study

1. To synthesize tungsten oxide thin films by sol-gel spin coating and electrochemical methods.

2. Investigating the Hydrogen sensing properties of gasochromic Pt/ Pt doped WO_3 samples and studying the effect of sol and doping concentrations

3. Investigating the effect of operating temperature on gasochromic performance and determining the lower detection limit for the optimized sample.

4. Studying the optical properties of tungsten oxide in aqueous solutions of Sodium chloride (in TRIS buffer and DI water) for Sodium ion detection and selectivity check against other alkali ions such as K^+ and Ca^{2+}.

5. Detailed material characterization was done to study the effect of structural changes on the gasochromic and Sodium sensing properties, and the corresponding data are correlated with transmittance measurements.

The thesis consists of six chapters. The **first chapter** highlights a review of different types of gas sensors and their advantages and disadvantages.

The **second chapter** discusses the sol-gel synthesis of Pt and Pd doped tunsgten oxide films. Detailed material characterization has been done and the effect of sol concentrations and doping are presented here.
In **third chapter** optical transmittance changes are reported for Pt and Pd doped samples at different operating temperatures. The dynamic response are measured at different Hydrogen concentrations and presented here. The correlation between gas sensing results and characterizaton results are also discussed.
The **forth chapter** describes electrochemical deposition of tunsgten oxide films from Peroxo Tungstic Acid precursor under different sol concentartions and deposition conditions. Detailed material characterization is also done for the samples and the same is preseneted in this chapter.
The **fifth chapter** focuses on Sodium sensing properties of electrodeposited tunsgetn oxide films based on optical transmittance changes.
Finally the **six chapter** presents summry, conclusion and future scope of the work.