Spectral Characterization of Tin Dioxide for Gas-Sensing Applications

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Abstract

Thin films and powder samples of tetragonal tin dioxide (SnO₂) on UV quartz and silicon wafers, created through radio frequency (RF) sputtering in an oxygen/argon mixed atmosphere, have been prepared and characterized spectroscopically. These thin films, along with SnO₂ powder samples, were analyzed using a variety of different spectroscopic techniques, including Raman spectroscopy, X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM). The spectral results have been compiled and analyzed in conjunction with a Molecular Dynamics simulation effort to model the vibrational modes of SnO₂. The primary goal of the project has been to compare the results of both experimental and computational approaches to detect spectral features that have not previously been recognized and predict potential uses of these vibrational features for gas-sensing technology.

Keywords: Tin dioxide, Raman spectroscopy, X-ray Diffraction, FTIR spectroscopy, SEM, Molecular Dynamics (MD) Simulation

Introduction

Thin films of semiconductor metal oxides (SMOs) are commonly used in gas-sensing applications due to their reusability, cost, and sensitivity to many dangerous gases. Our focus is on tin dioxide (SnO_2) as a gas sensor. N-type SMO, such as SnO2, will have their charge carriers (electrons) trapped by ambient oxygen (O_2) under normal atmospheric conditions. The lack of free charge carriers can be measured as a large increase in resistivity. In the presence of poisonous or flammable gases, such as H₂, CH₄, or CO, less charge carriers on the surface of the SnO₂ will be trapped, causing a decrease in resistivity. This change can be dramatic and easily detected (Wilson et al., 2018). These thin films usually operate best when heated to temperatures around 200 °C. If the film of SnO₂ is too thick, fluctuations in resistivity due to the presence of dangerous gases will be minimized, because much of the sample will be unaffected by atmospheric conditions. At the other extreme, a film too thin will not be able to detect any gases. Du and George (2008) showed that the maximum sensitivity occurs at the Debye length, which is close to 30 Angstroms for SnO₂. In our experiments, a range of film thicknesses were used, ranging from 41 to 908 nm. These relatively thicker samples allowed for easier viewing during the spectroscopic analysis. The thin films of tetragonal SnO2 on UV quartz and silicon wafers were created through radio frequency (RF) sputtering in an oxygen/argon mixed atmosphere. SnO_2 powder of 99.9 percent purity from the same supplier was also analyzed. The powder was chosen due to its high level of purity. Spectroscopic features exclusive to SnO₂ can be determined with this type of sample. SnO₂ has 8 different vibrational modes (Degler, 2017); of which 4 are infrared (IR) active and 4 are Raman active. The B1g Raman active mode was not expected to be visible to the Raman spectrometers used in the experiment. Eg, close to 475 cm⁻¹, represents the translational mode of SnO₂; A_{1g}, close to 630 cm⁻¹, represents the symmetric O-Sn-O stretching mode, B_{2g}, close to 774 cm⁻¹, represents the antisymmetric O-Sn-O stretching vibration (Ferreira, 2015)(Sergent et al., 2006).

Methodology

All the samples were measured at room temperature using the 780, 532, and 514 nm laser excitation Raman spectrometers. The powder was measured at varying temperatures between 30 and 170 °C. The samples were measured by FTIR in both the mid (450-4000 cm⁻¹) and far (150-1800 cm⁻¹) IR range. The powder was measured using an Equinox 100 XRD.





Fig. 1(a): Raman spectra of powder SnO_2 in the temperature range 30-170 ^oC (left). Fig. 1(b): X-ray diffraction spectra of SnO_2 powder sample at room temperature (right).

The E_g , A_{1g} , and B_{2g} modes (Nehru, 2014) are all clearly distinguishable, as shown in Fig. 1 (a). All of the peaks were redshifted with increased temperature. The E_g feature notably had the lowest rate of change and was reliably found between 475.8 and 473.9 cm⁻¹. The A_{1g} peak was recorded in the range 634.4-631.1 cm⁻¹, while the B_{2g} peak had much noisier values, and was visible in the interval 776.2-772.9 cm⁻¹. There are also some novel features visible around 545 and 690 cm⁻¹. The XRD data shown in Fig. 1(b) does more than simply validate the identity and structure of the sample. The well-known Scherrer equation yields the average particle size, D, around 4.12 Angstroms.

References

Degler, David. (2017). Spectroscopic Insights in the Gas Detection Mechanism of Tin Dioxide Based Gas Sensors.

Ferreira, Carlos Sergio; Santos, Pamyla Layene; Bonacin, Juliano Alves; Passos, Raimundo Ribeiro; Pocrifka, Leandro Aparecido.(2015). Rice Husk Reuse in the Preparation of SnO₂/SiO₂Nanocomposite. Materials Research, 18(3), 639-643.

Nehru, Lajapathi Chellappan; Sanjeeviraja, Chinnappanadar. (2014). Rapid synthesis of nanocrystalline SnO₂ by a microwave-assisted combustion method. Journal of Advanced Ceramics, 2014, 3(3): 171-176. Sergent, N., Epifani, M. and Pagnier, T. (2006), In situ Raman spectroscopy study of NO₂ adsorption onto nanocrystalline tin (IV) oxide. J. Raman Spectrosc., 37: 1272-1277.

Wilson, R.L.; Simion, C.E.; Blackman, C.S.; Carmalt, C.J.; Stanoiu, A.; Di Maggio, F.; Covington, J.A. (2018). The Effect of Film Thickness on the Gas Sensing Properties of Ultra-Thin TiO₂ Films Deposited by Atomic Layer Deposition. Sensors 2018, 18, 735.

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