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Monitoring Surface Stoichiometry, Work Function and Valance Band of Tungsten Oxide (WO3), Molybdenum Oxide (MoO3) and Tin Oxide (SnO2) Thin Films as a Function of Temperature and Oxygen Partial Pressure with Advanced Surface Sensitive Techniques for Chemical Sensing Applications

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Atomic layer deposition (ALD) is a chemical vapor deposition (CVD) deposition method in which high-quality, fine functional oxide films in the range of 10-1000 nm can be grown. The low deposition temperature and nonobligatory of heat treatment make it possible to obtain fine grains with high surface area. Despite the fact that few reports in recent years highlighted the importance of thickness/microstructure [1], the role of the defect sites, electronic and surface properties have not been well characterized with varying temperature and oxygen partial pressure [2], additionally understanding on chemisorbed oxygen species and oxygen vacancies (V_O^(°°)) which facilitates the replenishment of chemisorbed oxygen ions on the surface [3] are also lacking. This report focus on a correlation of surface electronic, structural and chemical properties with the surface reactivity and sensing behavior of the ALD layers of tungsten oxide (WO3), molybdenum oxide (MoO3) and tin oxide (SnO2) in the thickness range of 20-100 nm by employing advanced synchrotron based surface sensitive spectral-microscopic techniques; near ambient x-ray photoelectron spectroscopy (NAP-XPS), x-ray induced photoelectron emission microscopy (XPEEM), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and low energy electron microscopy (LEEM). The characterization work is supported by extensive chemical sensor testing and electrical resistivity measurements.
Depletion layer, dissociative adsorption of oxygen, chemisorption and the continuous replenishment on the surface in the course of catalytic oxidation reactions are prerequisite for an explanation for sensing mechanism, indeed sustained operation for the metal oxide based chemical sensors. This work will focus on the stoichiometry, crystal structure, work-function (Φ), valance band, and surface defect analysis, oxidation state as a function of oxygen partial pressure and temperature and its effect on chemisorbed oxygen ion concentration, thin film processing conditions, microstructure/porosity, depletion layer and Schottky barrier height. Inorganic materials, particularly salts and oxides, are sensitive to photon induced damage, after prolonged high intensity x-ray exposure, on the other hand, it is required high enough intensity and spectral resolution (achievable in synchrotron sources 0.1-0.2 eV) to realize the proposed goals. PM4 with its low dose x-ray ability and SMART with its XPEEM capability end stations, at BESSY II, Berlin and unique NAP-XPS system at Charles University, Prague, enabled spectra-microscopic characterization with abovementioned techniques. The results are enclosed here briefly in Figure 1.
Figure1-a shows the valence spectrum of WO3 thin film extends up to the Fermi level starting after 250℃, indicating a change in the character of the sample surface together with electrical resistivity measurements. Figure 1-b shows bright-field image of the 700 ℃ deposited WO3 sample. As the figure reveals the formation of continuous thin film with homogeneous grain structure over the surface differentiating with the grain size as the thin film possesses larger grains and obviously higher surface roughness. In LEEM images contrast is determined by work function (Φ) variation over the surface. Surface topography, grain boundaries, porosity and stoichiometry can affect the work function (Φ). The variation in the work function (Φ) from grain to grain is higher in comparison to 600℃ deposited sample. In order to have better understanding on this, XPEEM analysis was conducted (not included here). The Figure 1-c shows a valance band spectrum of defective MoOx taken with 65 eV photons with two different take-off angles. Efermi level followed by valance band minimum, and at larger binding energies, O 2s was seen in the figure. Another feature observable is the 4d and 5s of Mo blended in between 5-12 eV. It is detected that the band gap is not entirely free of states due to the nonstoichiometry of the MoOx thin film. The oxygen vacancies (V_O^(··)) give rise the defect states located around ~3 eV below the Efermi level in 60° in comparison to the 0°. This is attributed to a change in occupancy of the Mo 4d and 5s bands due to reduction from Mo+6/Mo+5 to Mo4+. The valence band minimum is located at about 1.0 eV below the Fermi level.

Summary

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