SURFACE VALENCE STATE AND PHASE STRUCTURAL ANALYSIS OF NANOSTRUCTURED WO_3

J. Puustinen, J. Huotari and J. Lappalainen

Faculty of Information Technology and Electrical Engineering, P.O.B. 4500, FIN-90014 University of Oulu, Finland
email: jpuust@ee.oulu.fi

Nanostructures of WO_3 were grown using pulsed laser deposition in vacuum at room temperature and in partial oxygen pressures $p(O_2)$ varying from 0.08 mbar to 0.5 mbar. Laser fluence on the ceramic target was varied between 0.8 J/cm^2 and 2 J/cm^2. After the deposition films were post-annealed at temperatures of 400 °C - 600 °C. The exact microstructure was studied by X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM). The chemical valence states of the sample surfaces were analyzed using x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS).

The higher oxygen pressures induce agglomeration of nanoparticles in the plasma plume. These agglomerates grow on the substrate with exact growth apexes, leading to formation of WO_3 fractals with distinct tree-like structures that maximize the effective surface area of the films. The fractal dimensions D_f, deduced using Kaye method, of the samples varied from 2.25 all the way to 2.66, which indicate high fractal state of the samples. As the necking area between the particles in agglomerates is small due to open structure, post-annealing has minimal effect on the particle size, ranging from ~12 nm to 22 nm. At oxygen partial pressures used, the samples crystallized already at RT in PLD process, with both γ-WO_3 and ε-WO_3 phases present. At partial oxygen pressure of 0.08 mbar, the γ-WO_3 was highly preferred in the samples, while at pressure of 0.2 mbar the ε-WO_3 was highly preferred. As the post-annealing temperature increased from 500 °C to 600 °C the amount of γ-phase in the samples clearly increased with orientation towards [100] crystal directions, while the amount of ε-phase diminished. The changes in the lattice parameters of the monoclinic structures was seen to be minimal as the post-annealing temperature increased, only the β-angle showed greater deviations compared to theoretical values.

XPS results showed that, the chemical valence states of the films mainly consisted bulk tungsten ground states with no significant changes in binding energies in films with different post-annealing temperatures. These valence states do not have so significant effects on the chemical sensing mechanism, while the growth mode of microstructure and surface valence states of the samples probed by UPS dictate the sensing process.