Abstract

Growth process and parameters have a strong influence on tungsten oxide thin film characteristics. Films grown by different techniques show different structural, morphological and even chemical differences with each other. In an attempt to grow tungsten oxide thin films on a large scale at low cost with low impurity to meet the industrial demand mostly for electrochromic devices and gas sensors, a process-modified hot filament chemical vapor deposition system was used. The basic objective of this work was to study the film quality under different growth conditions. Finally, the work also concentrates on the formation of nanostructures and their growth mechanisms from these thin films.

The modification of the process in HFCVD based tungsten oxide thin film growth involves elimination of any organic precursor for tungsten oxide such as $W(CO)_6$ or alcoxides, thereby improving the purity and using the hot tungsten filament itself as a source for tungsten. This produces tungsten oxide in a controlled oxygen atmosphere. As a result, production cost decreases and the filament architecture can allow large deposition area. In the present study, with a helical filament from Edwards (ordering no. H014-01-022), a circle of diameter 2.8 inches can be deposited uniformly and the optimized pressure for deposition was around 300 – 400 mTorr.

As the pressure has a critical value for the growth procedure above which film growth is uncontrolled, the other parameters like substrate temperature were varied from room temperature to $430^{O}C$ at an interval of $100^{O}C$, while maintaining the pressure at around 380 mTorr. The influence of the substrate temperature on the structural and optical properties of the WO_3 films was studied. X-ray diffraction and Raman spectra show that as substrate temperature increases the film tends to crystallize from the amorphous state and the surface roughness decreases sharply above $230^{O}C$ as confirmed from AFM image analysis. Also from X-ray analysis it is evident that the substrate orientation plays a key role in growth. There is a sharp peak for samples grown on Si substrates due to texturing. The film thickness also decreases as substrate temperature increases. UV visible spectra show that as substrate temperature increases the film property changes from metallic to insulating behavior due to changing of stoichiometry, which was confirmed by XPS analysis, too. The overall results closely match with the films grown by other CVD methods.

Oxygen annealing effect on the tungsten oxide films deposited on the glass substrate by modified HFCVD was also studied. TEM investigations of the as-grown material show that most of the material is amorphous and there are few nanoparticles with sizes in the range of 6 nm. Applying the Scherer formula to the X-ray diffraction pattern, it was determined that after annealing in oxygen environment, crystallite size increases to 12 nm, which was also confirmed by TEM. XRD patterns confirm polycrystallinity in the annealed film for glass substrate as they show multiple orientations of growth. FTIR spectra show increase of crystallinity as annealing temperature increases. According to AFM image analysis, as the annealing temperature increases film surface becomes much more rough. UV-visible absorption spectroscopy indicates a blue shift in the spectrum maxima as the annealing temperature increases.

Various low dimensional structures such as rods, whiskers, ribbons, sheets or platelets have also been grown by simple annealing of WOx thin films on Si (100) substrate. The formation of different surface morphologies has been studied with the variation of annealing temperatures, annealing time and for different thicknesses of tungsten oxide films. X – ray diffraction was performed on the samples to determine the phases, along with Raman spectroscopy. Transmission electron microscopy, scanning electron microscopy and optical microscopy were used to visualize the structures. Humidity played a crucial role in determining a particular phase and structure, whereas thickness of the original film controls the density of the nanostructures as well as the size of the nano/micro-structures. Two models have been formulated for the growth of two different nano-structures and a preliminary attempt on template based growth for vertical structures showed the potential of the technique.