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Microstructural evolution of tungsten oxide thin films

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ABSTRACT

Tungsten oxide thin films are of great interest due to their promising applications in various optoelectronic thin film devices. We have investigated the microstructural evolution of tungsten oxide thin films grown by DC magnetron sputtering on silicon substrate. The structural characterization and surface morphology were carried out using X-ray diffraction and Scanning Electron Microscopy (SEM). The as deposited films were amorphous, where as, the films annealed above 400 °C were crystalline. In order to explain the microstructural changes due to annealing, we have proposed a ''instability wheel'' model for the evolution of the microstructure. This model explains the transformation of mater into various geometries within them selves, followed by external perturbation.

1. Introduction

Research on the physical and chemical properties of nano-structured materials have attracted increasing interest due to potential applications of such structures in many future devices. In particular, thermal stability of nano-structured material is necessary for their implementation in nano-scale devices. Due to high surface to volume ratio, nano-structured materials become unstable with external perturbation (particularly at elevated temperatures when the mobility of atoms by diffusion is higher). In 1D the classic examples being the nano-wires fragments due to Rayleigh instability when exposed to high temperatures. The nano-wires driven by Rayleigh instability undergo various configurational changes and finally break up into a chain of spheres at temperatures well below the melting point [1–4]. While in 2D thin films, the stability of the film is modified at high temperature relating to its shape change and the continuous film breaks up into a group of islands [5–7].

In this study, we present the evolution of microstructure in case of tungsten oxide thin films due to annealing. Tungsten oxide (WO_3) is a material with a large potential for use in many practical applications such as ''smart'' electrochromic windows and switchable devices [8,9]. It is highly sensitive even to very low concentrations of toxic gases such as NO_x, H_2S, NH_3, ozone, CO_2, SO_2 [10–14]. Hence it is also potential candidate for sensitive for environmental monitoring.

Application of annealed WO_3 films in gas sensors has two major problems. High temperature annealed films exhibit larger cracks and high surface roughness. Due to larger cracks, the carrier mobility is drastically reduced and hence the response time of gas sensors would increase to a few minutes. Furthermore, patterning of these films using microlithography becomes difficult due to high surface roughness. The other major issue of these films is the instability of microstructure at high operation temperatures for long periods. The latter phenomenon is mainly due to the diffusion and coalescence of grains during heating for a long period [15].

Conventionally WO_3 films are prepared by sol gel [16], pulsed laser deposition [17], thermal evaporation [18], electron beam evaporation [19], and sputtering [20]. However, the advantage of reactive magnetron sputtering for this purpose is mainly due to the high deposition rate by sputtering from metallic target, which also enables control of the stoichiometry of the deposited films.

In this paper we present our investigations on evolution of microstructure of WO_3 thin film due to annealing on silicon substrates. Based on our observations, a model has been proposed relating to the stability of the microstructures.

2. Experimental

Tungsten oxide thin films were deposited on p-silicon ⟨1 0 0⟩ substrates using reactive magnetron sputtering with high pure oxygen (99.99%) partial pressure of 8×10^{-4} mbar along with high pure argon (99.99%), the total pressure being 4×10^{-3} mbar. The sputtering chamber was evacuated to a base pressure of 2×10^{-5} mbar before admitting the gases.

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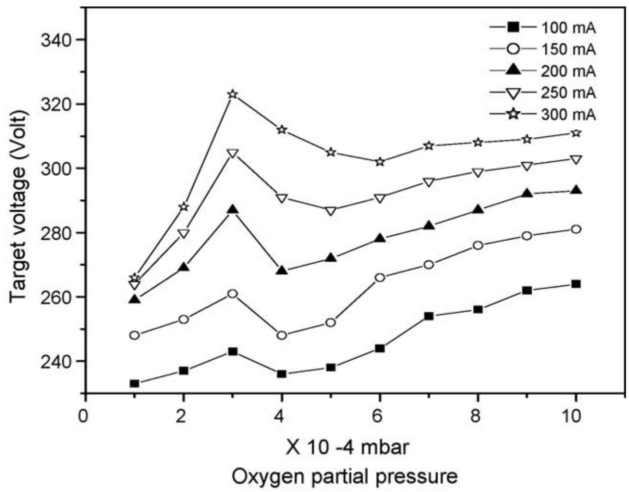

Fig. 1. Variation of target voltage as a function of oxygen partial pressure.

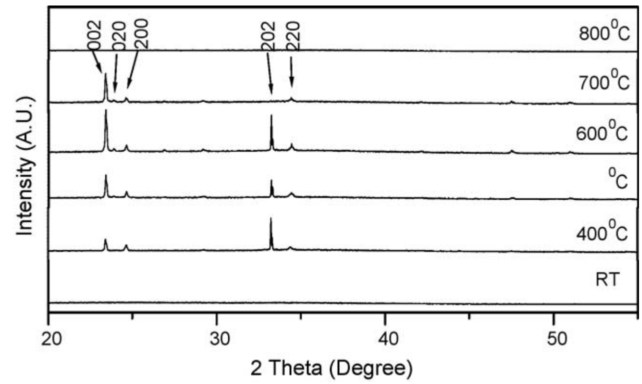

Fig. 2. XRD pattern of the WO_3 thin films prepared at different annealing temperatures.

The silicon substrates were subjected to standard cleaning procedures before introducing into the deposition chamber. A planar and circular tungsten disk of 99.99% purity and 100 mm diameter was used as the target. The substrate to target distance was maintained at 110 mm.The deposition was done at a discharge current of 250 mA. Some samples were annealed in ambient for 30 min in the temperature range of 300–800 °C.

3. Results and discussion

3.1. Glow discharge characteristics

In order to optimize the region where the tungsten oxide thin films can be prepared, the glow discharge characteristics of reactive sputtering were studied under different oxygen partial pressures. The dependence of oxygen partial pressure on the applied target voltage to obtain constant current is interesting. It qualitatively can predict the nature of the deposited film. When the target current is maintained constant, the characteristics show that the voltage increases initially, reaches a maximum at a particular oxygen partial pressure and later decreases upto certain pressure, and then almost remains constant as shown in Fig. 1. This behaviour has been explained earlier by Mohan Rao and Mohan [21] in their model of reactive sputtering process. The ideal region for the deposition of oxide films with reasonable deposition rates is the region where the cathode voltage remains almost constant. Based on these results, during the present study, all the oxide films have been deposited with a discharge current of 250 mA and an oxygen partial pressure of 8×10^{-4} mbar.

3.2. Crystal structure

The structure of the samples was characterized by X-ray diffraction with Cu Kα radiation and the diffraction pattern is shown in Fig. 2. The films grown at ambient temperature did not show any crystallinity, but with annealing at 400 °C, the monoclinic phase appears as seen from the diffraction pattern. With annealing at higher temperatures, monoclinic phase is retained and this behaviour is similar to that reported earlier [19,22]. With increase in annealing temperature, the intensity of 0 0 2 peak increases with simultaneous decrease in 2 2 0 peak

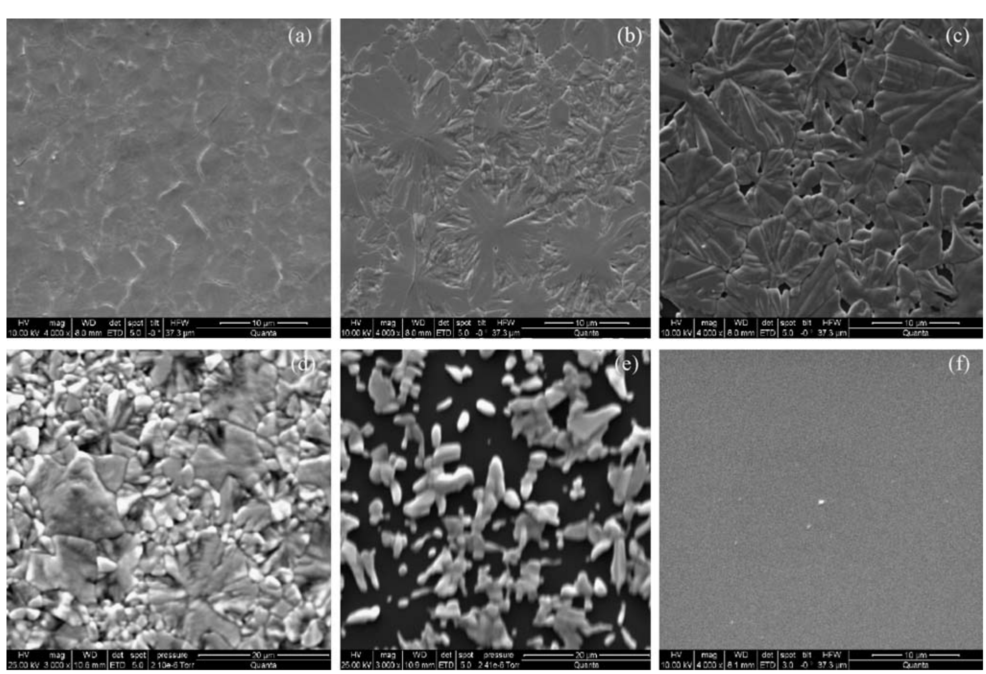

Fig. 3. SEM images of WO_3 thin films prepared at different annealing temperatures. (a) Room temperature, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, (f) 800 °C.