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Tuning Stoichiometry and Structure of Pd-WO_{3-x} Thin Films for Hydrogen Gas Sensing by High-Power Impulse Magnetron Sputtering

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Abstract: By tuning the deposition parameters of reactive high-power impulse magnetron sputtering, specifically the pulse length, we were able to prepare WO_{3-x} films with various stoichiometry and structure. Subsequently, the films were annealed in air at moderate temperature (350 °C). We demonstrate that the stoichiometry of the as-deposited films influences considerably the type of crystalline phase formed in the annealed films. The appropriate sub-stoichiometry of the films (approx. $WO_{2.76}$) enabled crystallization of the monoclinic phase during the annealing. This phase is favorable for hydrogen sensing applications. To characterize the sensory behavior of the films, the tungsten oxide films were decorated by Pd nanoparticles before annealing and were assembled as a conductometric gas sensor. The sensory response of the films that crystallized in the monoclinic structure was proven to be superior to that of the films containing other phases.

Keywords: tungsten oxide; WO_3; hydrogen sensing; conductometric gas sensor; HiPIMS; stoichiometry

1. Introduction

Hydrogen is a reliable and prospective source of energy because of its clean and renewable essence. The growing hydrogen industry puts pressure to develop new hydrogen sensors associated mainly with hydrogen mobility and energy storage. Cheap, reliable, and greenway syntheses are desired as well as well-performing materials which include applications not only to hydrogen storage and production but also to hydrogen sensing for security and/or performance monitoring.

Metal oxide semiconductors (MOSs) are the most used class of sensing materials due to their diverse composition, tunable bandgap properties, possible nanostructuring, and high chemical stability. They have been widely studied for being used as conductometric sensors, where the change of resistivity upon hydrogen presence was monitored [1,2]. Among MOSs, tungsten oxide (WO_3) has attracted attention for the last few decades because of its interesting electrical, structural, and chemical properties [3,4]. Pure WO_3 can easily detect oxidizing gases such as NO_2, SO_2, O_3, etc. [5–10], but more challenging is an enhancement of its sensitivity towards reducing gases (H_2, CO, NH_3, etc.). This can be done by the loading of WO_3 material by noble catalysts such as Au, Pt, and Pd [1,3,11–13].

Magnetron sputtering is a deposition technique that enables the microstructure to be controlled and the physical properties of the films to be tuned [14]. Reactive magnetron sputtering is popular because it is capable of producing compound films (including MOSs) with various stoichiometries and structures [15–17]. Among a wide variety of magnetron sputtering techniques, reactive high-power impulse magnetron sputtering (HiPIMS) is a prominent technique for the preparation of high-quality compound films. During the process, a reactive gas (e.g., O_2) is dissociated, which improves its

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