ABSTRACT

The doctoral dissertation concerns the study and analysis of the selected properties of mixed copper and titanium oxides (CuTi)Ox thin films deposited using magnetron sputtering that can be applied as a hydrogen gas sensors. In such thin films the resistance value can be reversibly changed upon interaction of adsorbed gas molecules at their surface. Nowadays, the production of gas sensor devices is a key issue for the sake of the growing demand of controlling harmful and flammable gases in the environment and in industrial process.

Hydrogen is a colourless and odourless gas that is widely used in many industries such as the food, chemical, metallurgical and petrochemical industries. It is referred to as the 'fuel of the future', but due to its high diffusion coefficient and flammability, it can be hazardous to human health and life. For safety reasons, with the development of hydrogen-based technologies, the development of hydrogen sensors is also fundamental.

Metal oxides commonly used as gas sensors (SnO_2, TiO_2, ZnO) are mostly n-type semiconductors, however also p-type semiconductors such as copper oxides or nickel oxides are worth to investigate. A fairly common procedure to develop a reliable gas sensors involves creation of heterostructure materials compose of two or more metal oxide e.g. SnO_2-TiO_2. This work is dedicated to mixed copper and titanium oxides in which copper and titanium concentration varies over wide range. The fundamental properties (microstructure, optical or electrical properties) of e.g. 50 at. % of Cu_xO and 50 at.% of TiO_x mixtures are not well established. The lack of thorough studies were one of motivations to undertake this topic. Moreover, such structures have a great potential to apply them in gas sensing technology.

In the Team of Thin Films Technologies, six mixed mixtures with copper content in the mixture ranging from 0 to 100 % at. Cu were deposited using magnetron sputtering in oxygen deficiency conditions and annealed at temperatures of 200°C, 250°C and 300°C to cause only partial copper and titanium oxidation. Also reference TiO_x and Cu_xO were investigated. The aim of this thesis was also to determine the influence of factors such as material composition, microstructure and surface properties of the films on the hydrogen detection performance. Measurements of the sensing response of the films at different temperatures and for different hydrogen concentrations (100-1000 ppm) enabled the determination of hydrogen detection mechanisms in resistive gas sensors based on (CuTi)Ox mixtures.

Scanning electron microscope imaging was used to characterise the morphology of the (CuTi)Ox thin films. The annealing process resulted in significant changes in the roughness of the thin films and the formation of nanowires visible on the surface of the material. Using a grazing incidence X-ray diffraction method, changes in the crystalline structure of the (CuTi)Ox thin films were observed, allowing the development of a simplified phase diagram of the Cu-Ti-O system. Copper and titanium oxides exhibit opposite types of electrical conductivity, but the (CuTi)Ox mixtures were semiconductors with a strong hole type of electrical conductivity. This made it possible to study, so far poorly understood, sensing properties of metal oxide thin films with a hole type of conductivity. Mixtures of copper and titanium oxides showed a higher sensitivity to hydrogen than the reference thin films of Cu_xO and TiO_x. The optimum operating temperature of the (CuTi)Ox layers was also determined, at which the sensing responses significantly exceeded those presented in the literature for copper-titanium oxide-based structures. The comprehensive characterisation of the thin films also included studies performed by X-ray photoelectron spectroscopy and in-situ studies with hydrogen. Oxides present on the surface of the films were identified and the reduction of TiO_2 to Ti_2O_3 and CuO to Cu_2O oxides resulting from hydrogen interactions with the surface of the thin films was studied. Based on the extensive characterisation of (CuTi)Ox thin films, a proposal for a mechanism for hydrogen detection by these materials was developed.

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