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Ultrathin SnO_2 gas sensors fabricated by spray pyrolysis for the detection of humidity and carbon monoxide

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ABSTRACT

A new gas sensor based on ultrathin SnO_2-films with high sensitivity for humidity and carbon monoxide has been developed. The SnO_2-sensing films are fabricated by a spray pyrolysis process with a thickness between 50 and 100 nm on oxidized silicon substrates. The SnO_2-sensing films are finally processed in arrays of parallel bars to achieve the sensor device. The structure of SnO_2-layers has been characterized by SEM, AFM and XPS analysis. The sensors are operated at temperatures of 250–400 °C, show high sensitivity to humidity and are able to detect carbon monoxide down to a concentration of less than 5 ppm. The fabrication process of the gas sensor is fully compatible with silicon process technology. The spray pyrolysis technique is a simple and flexible process and thus is suitable for the cost efficient fabrication of a new gas-sensing device. Strategies to improve sensitivity and selectivity of the sensor toward different gas species are discussed.

1. Introduction

Triggered by various applications like industrial process control, safety systems, environmental monitoring, or disease diagnostics in medicine, there is an increasing demand for gas sensing devices. A number of different gas sensors based on different sensing materials and measurement principles have been developed over the years. Especially metal oxides have become established sensing materials for a number of applications [1–5]. Metal oxide gas sensors rely on changes of electrical conductance due to the interaction with the surrounding gas. Due to their high chemical resistance and thermal stability, metal oxides are suitable for measurements in harsh environments. Among all sensing materials, SnO_2 is the most prominent candidate, and many SnO_2-based sensor devices have been realized so far [6–12].

Development of metal oxide gas sensors has been strongly driven by the implementation of MEMS technology. Thermally insulated micro-hot plates, for example, have been employed as platforms on CMOS-chips for the realization of sensor arrays. The arrays comprise different polycrystalline sensor materials and are held at different temperatures to provide a certain level of selectivity [13–17]. A most powerful strategy to improve sensor performance is the implementation of nanostructured materials, which have a high surface to volume ratio and thus a strong interaction between the surrounding gas and the material. Several sensor devices utilizing nanocrystalline metal oxide films have been realized so far [4,18,19]. Devices incorporating single-crystalline nanobelts and nanowires as sensing probes have also been demonstrated [20]. For example, nanobelts and nanowires of SnO_2 and In_2O_3 [21,22], and single-walled carbon nanotubes [23] have been fabricated for sensing of environmental polluting species like CO, NO_2 and NH_3.

We report on new gas sensors based on ultrathin nanocrystalline SnO_2-films, which are fabricated by a spray pyrolysis process on silicon substrates with a thickness between 50 and 100 nm. The planar SnO_2-films are processed in arrays of parallel bars by means of semiconductor technology. At operation temperatures of 250–400 °C the sensors are able to detect humidity and carbon monoxide. CO can be detected down to a concentration of less than 5 ppm, which demonstrates the superior sensing properties of ultrathin SnO_2-films as compared to conventional sensor structures. The spray pyrolysis technology is a well-known method for the deposition of a wide variety of thin films and has been used for decades in the glass industry [24] and in solar cell production [25]. Spray pyrolysis is a simple and flexible deposition process, which requires no vacuum and offers an easy technique for preparing films of various compositions [26–30]. The method has been employed for dense films, porous films and for powder production [31]. We demonstrate that the spray pyrolysis technology is also suitable for the cost efficient fabrication of ultrathin nanocrystalline SnO_2-films for gas sensing devices. In the present work the fabrication process

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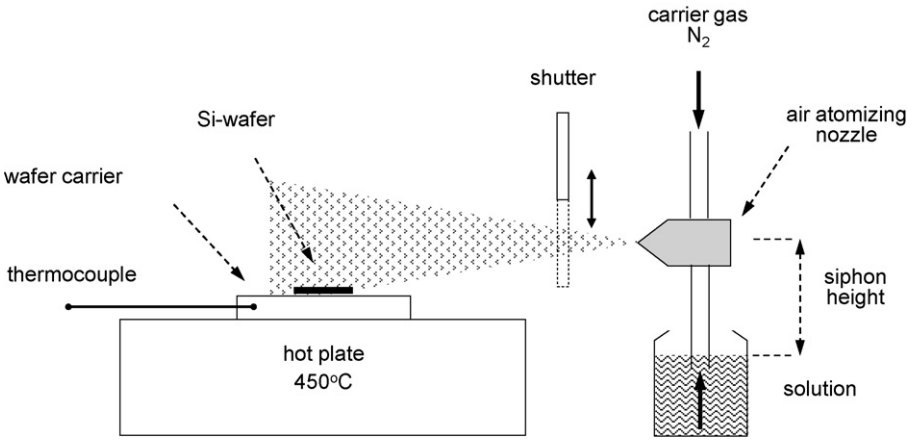

Fig. 1. Setup of spray pyrolysis process for parallel flow of atomized spray.

of the sensor, the surface analysis of the SnO_2 films, as well as the electrical characterization and the gas sensing performance of the detectors are described in detail.

2. Theory

The sensing mechanism of thin film metal oxide gas sensors is related to ionosorption of gas species over their surfaces, which leads to charge transfer between gas molecules and the surface and thus to changes of the electrical conductance. The expected response of thin SnO_2-films to CO and humidity is as follows.

The normal operation temperature of SnO_2-gas sensors is in general within the range of 200 and 500 °C, where conduction is electronic and oxygen vacancies are doubly ionized. The most important ionosorbed species when operating in ambient air are oxygen and water. In the temperature range between 100 and 500 °C oxygen is ionosorbed on SnO_2 in a molecular (O_2^-) and atomic form (O^-). Since O_2^- has a lower activation energy it dominates up to about 200 °C, while at higher temperature the O^- form dominates [32,33].

For a reducing gas, such as CO, gas detection is related to the reactions between CO and ionosorbed surface oxygen. The adsorbed CO molecules oxidize to CO_2 by consuming negatively charged O^-, where the electron is transferred to the surface and increases the electrical conductance of the SnO_2-film. The opposite process would occur for an oxidizing gas.

The response to humidity is more complex. Three models have been developed to explain the experimentally reported increase of conductance [34,35]. The interaction with water leads to molecular water and hydroxyl group adsorption. While the OH groups bound to Sn-atoms form isolated hydroxyl groups, the OH^+-groups incorporating lattice oxygen act as ionised donors and contribute the electrons. Another possibility is the reaction between hydrogen atoms and lattice oxygen and subsequent binding of the resulting hydroxyl groups to the Sn-atoms. The resulting oxygen vacancies are ionized and account for the additional electrons [36]. The third model suggests an indirect effect, such as the interaction between the hydroxyl group or the hydrogen atom with an acceptor surface state. Also pre-adsorbed oxygen might be rearranged in the presence of adsorbed water, which has donor properties [37–39].

3. Experimental

The sensors are based on nanocrystalline SnO_2-films, which are fabricated by a spray pyrolysis process: a 0.28 molar solution of tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and ethyl acetate ($C_4H_8O_2$) is sprayed on Si-substrates with a 750-nm thick SiO_2 layer on top, which are heated to a temperature of 450 °C. Tin oxide is formed according to

$$SnCl_4 + 2H_2O \leftrightharpoons SnO_2 + 4HCl \quad (1)$$

The experimental setup (Fig. 1) consists of a 30 cm × 30 cm hot plate, where the samples are placed, and a siphon-fed spray setup with an air atomizing spray nozzle (QuickMist QMJML, Spraying Systems Co.) and a round air cap. N_2 with a pressure of 0.8 mbar is used as a carrier gas; a siphon height of 10 cm results in a solution flow rate of 10 ml/min.

Spray pyrolysis has been performed in two configurations: in a first setup the nozzle was positioned above the hot plate, so that the atomized spray was flowing perpendicular to the sample. In subsequent experiments the nozzle was positioned on the side of the hot plate (setup shown in Fig. 1), allowing the atomized spray to flow parallel to the surface. Distance to the samples is 20 cm. Samples are placed on the hot plate and after preheating for 5 min the spray pyrolysis process is started. A mechanical shutter between spray nozzle and sample is used to precisely control the spraying process duration. The shutter is opened 5 s after starting the carrier gas flow to eliminate bigger droplets, which specifically form at the beginning of the spray process.

Dependence of film thickness on spray duration for both setups (perpendicular and parallel flow) is shown in Fig. 2. Thickness of the films is measured with an interferometer (Model 210 NanoSpec/AFT). It was found that the parallel flow configuration allows better thickness control and avoids the emerging of

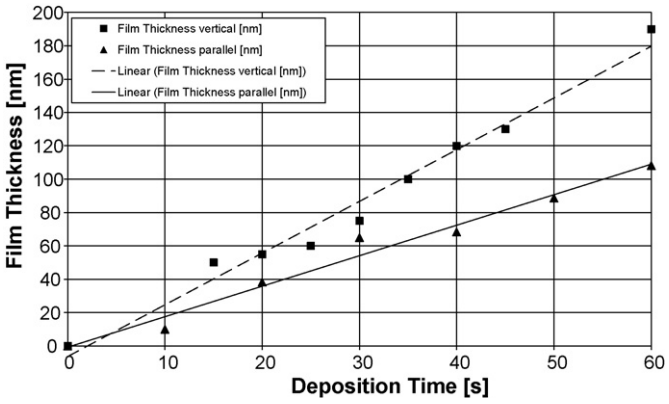

Fig. 2. Film thickness vs. deposition time for perpendicular and parallel atomized spray flow.