Rational design and development of room temperature hydrogen sensors compatible with CMOS technology: a necessary step for the coming renewable hydrogen economy

J. Kosto¹, R. Tschammer¹, C. Morales¹, K. Henkel¹, C. Alvarado², I. Costina², M. Ratzke³, C. Wenger², I. Fischer³, J. I. Flege^{*1}

¹ Brandenburgische Technische Universität Cottbus-Senftenberg, FG Angewandte Physik und Halbleiterspektroskopie, 03046 Cottbus, Germany,

² IHP – Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany,

³ Brandenburgische Technische Universität Cottbus-Senftenberg, FG Experimentalphysik und funktionale Materialien, 03046 Cottbus, Germany

*flege@b-tu.de

Summary:

The transition towards a new, renewable energy system based on green energy vectors, such as hydrogen, requires not only direct energy conversion and storage systems, but also the development of auxiliary components, such as highly sensitive hydrogen gas sensors integrated into mass devices that operate at ambient conditions. Despite the recent advances in nanostructured metal oxide thin films in terms of simple fabrication processes and compatibility with integrated circuits, high sensitivity, and short response/recovery times usually require the use of expensive noble metals or elevated temperatures (>250 °C), which results in high power consumption and poor long-term stability. This article presents the first steps of the work on developing a novel resistive hydrogen gas sensor based on ultrathin cerium oxide films, compatible with complementary metal oxide semiconductor technology and capable of operating at room temperature. Here, we show a multidisciplinary bottom-up approach combining different work areas for the sensor development, such as sensor architecture, sensing mechanism and deposition strategy of the active layer, electrical contact design depending on the desired electrical output, and fast testing under controlled environments.

Keywords: Ceria, gas sensor, hydrogen, ALD

Introduction

In the last decades, the world has realized that we are facing an ecological crisis tightly linked to irreversible climate changes and the depletion of fossil fuels, caused by human activities. One of the ways to create a sustainable future for our planet is the transition towards green, renewable energy sources that decrease greenhouse gas emissions. Hydrogen (H₂) is a promising new energy vector due to its high abundance in nature and high combustion efficiency, defining the H₂ economy. However, using hydrogen presents safety drawbacks: at ambient pressure, the H₂/air mixture is explosive when H₂ concentrations exceed 4%. Thus, it is necessary to develop reliable and cheap H₂ detection methods for ensuring safety in H₂ production, transport, and storage.

Nowadays, many different H_2 sensors rely on the physicochemical interaction between the sensing material and H_2 . One of the most common types are resistive sensors based on reactive metal oxides since they are easy and inexpensive to manufacture, feature fast response/recovery time, and have high stability and sensitivity. However, most of them require elevated operation temperatures (250-500 °C), have low selectivity, and are vulnerable to humidity [1-2]. Together with necessary device miniaturization and CMOS compatibility, these challenges need to be solved to enable their use in mass devices.

Typically, oxides of Zn, Sn, In, Cu, and W are used in H₂ sensing [3]. Different possibilities have been explored to increase the response strength and decrease the response time while reducing the sensor working temperature. Firstly, the surface-to-volume ratio can be increased. In this regard, thin films are often used due to their small thickness and large lateral size, as well as mesoporous and nanostructured deposits [4]. A promising alternative in terms of synthesis control would be the deposition of conformal and homogeneous ultrathin films (<20 nm) on nanostructured Si-based substrates. Secondly, catalytic noble metals such as Pt or Pd [5] can be used. Thus, the design of novel metal oxide-based resistive H₂ sensors requires (i) the synthesis and development of active sensing materials with high response at low temperatures (close to room temperature - RT) without the use of expensive catalysts, and (ii) the use of deposition techniques compatible with CMOS technology to ensure the growth of homogeneous films on nanostructured substrates.

Considering these two challenges, we propose using cerium oxide (CeO_x), which has shown moderate operation temperatures towards H₂ detection, particularly when combined with SnO_x and InO_x, as sensing material. The reason behind this is the facile exchange of cation oxidation states, Ce³⁺ and Ce⁴⁺, under reductive and oxidizing atmospheres, which is accompanied by creation or annihilation of oxygen vacancies and defects in the surface and bulk regions under varying redox environmental conditions, thus leading to changes in electrical conductivity. Ceria can easily be deposited by a variety of physical and chemical deposition techniques, ensuring precise control of crystallinity, microstructure, and composition to tailoring of its physicochemical properties and, thus, its response and selectivity to different gases.

This paper describes a multidisciplinary bottomup approach combining work from different research areas to develop a CeO_x-based resistive sensor for hydrogen detection. We will discuss design aspects of a nanostructured sensor with a conformal ceria active layer and the effect of electrode geometry, the latter supported by numerical calculations.

Experimental

All atomic layer deposition (ALD) processes were performed in a homemade ALD reactor combined with X-ray photoelectron spectroscopy (XPS) for in-situ analysis [6]. First, nanostructured SiO_x/Si wafers were coated with 5 nm of Al₂O₃ deposited by thermal ALD at RT using trimethylaluminum and H₂O as precursors. Then, CeO_x ultrathin films were prepared with the organometallic precursor tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV) (Ce(thd)₄) (Epi-Valence) and ozone (O₃/O₂) as co-reactant, reaching a steady growth of ~0.15 Å/cycle. Ozone was obtained from an ozone generator (Oxidation Technologies, LLC). The XPS tool was equipped with an Al/Mg dual anode X-ray source and a hemispherical analyzer (EA 125, Omicron). The thickness of the ultra-thin ceria layers was calculated from the attenuation of the Al 2p peak intensity. The oxidation state of cerium was determined from Ce 3d spectra, which were decomposed into five doublets (two corresponding to Ce^{3+} and three to Ce^{4+} states) [7]. The Ce^{3+} concentration was calculated as the intensity ratio between the Ce^{3+} peaks and the total Ce 3d level intensity. Transmission electron microscopy (TEM) and energy dispersive X-ray fluorescence (EDX) measurements were performed with a FEI Tecnai Osiris instrument operated at 200 kV.

The numerical simulations calculate solutions of the continuity equation for electric current using the Finite Element Method (FEM) (AC/DC module of "Comsol Multiphysics"), considering appropriate boundary conditions (electric potential, electrical insulation, contact resistances).

Results and discussion

Sensor geometry

The resistive metal oxide gas sensors are intended to allow the measurement of changes in the partial pressure of gases by tuning the electrical resistance of the active material. To achieve sufficiently high sensitivity of the sensor, we propose using an active metal oxide ultrathin (<20 nm) laver deposited on Si-based nanostructured substrates to increase the total surface-to-volume ratio of the active material in a controlled, reproducible way. Figure 1a shows a scheme of the nanostructured geometry, which includes an insulating layer (Al₂O₃) on the Si-based substrate and, the active ceria on top. Both, the Al₂O₃ and CeO_x, layers are deposited by ALD, which, thanks to its self-limiting nature, allows controlling the deposition on the atomic level, ensuring uniform and conformal growths on complex 3D geometries. Figure 1b) shows a cross-sectional TEM image of the nanostructured substrates together with the respective EDX chemical map taken for Si (red), AI (blue), and Ce (yellow) components, confirming that ceria was evenly and continuously deposited even in the corners of the 3D structure.

Materials characterization

Figure 2 depicts the in-situ XPS Ce 3d spectra of the ceria films after subsequent ALD cycles. After 50 cycles, i.e., ~0.4 nm, mostly Ce3+ is present (~90%), indicating a high level of reduction of the film that can be explained by (i) a significant amount of defects, (ii) an initial island-like morphology of the films, and (iii) the creation of aluminate species at the interface during growth. The Ce³⁺/Ce⁴⁺ ratio notably decreases with increasing oxide thickness, leading to almost 70% of Ce4+ in ~7.5 nm thick films (500 cycles). This dependence of the ceria oxidation state on thickness and film/substrate interaction can potentially be applied to adjusting the reactivity of the film and optimizing the multilayer design of the sensor.



Fig. 1. a) Cross-sectional scheme of a 3D nanostructured sensor geometry with ceria active layer; b) TEM image with the EDX image demonstrating conformity of the ceria layer deposited by ALD on Si-based nanostructured substrates.

Working electrode

A crucial factor influencing the efficiency of resistive sensors is the geometry of the working electrode since contact resistance depends on its area. Thus, the simulation-based optimization of the electrode geometry was done when scaling sensor dimensions to improve the effectiveness of the contacts.

The measured signal of the sensor is its electrical resistance. Thus, a change in the specific electrical resistivity (ρ) of the active layer due to a change in the detected gas concentration (Δ c) should lead to a significant relative change (Δ R) in the total resistance (R) of the structure. This relationship can be expressed as follows:

$$\frac{\Delta R}{R} = \frac{dR\Delta\rho}{Rd\rho} = \frac{dR}{Rd\rho} \cdot \frac{d\rho}{dc} \cdot \Delta c = G \cdot M_1 \cdot M_2 (1)$$

The material-dependent factors M_1 and M_2 are considered external and (slightly) variable; therefore, they do not allow for optimization at the current stage of the work. The geometrydependent term $G=(dR/Rd\rho)$ is accessible through modeling and will be considered in the following.



Fig. 2. In-situ XPS Ce 3d core level spectra taken from ALD ceria films of various thicknesses.

The expected currents are determined from the solutions of the continuity equation by integrating the current densities over the film thickness, thereby estimating the resistance R of the structure. The derivative appearing in equation (1) is approximated by central difference quotients in parameter-dependent studies of the form $R(\rho)$. Typical results for simulations considering fixed parameters (electrode spacing and specific resistivity of the oxide) and variable parameters (electrode width and contact resistivity) are depicted in Figure 3. Both graphs exhibit a similar trend in dependence of the contact resistance (at the moment, it cannot be experimentally achieved): up to a certain value, both device resistance and estimated sensitivity show no influence, while above it, larger contacts exhibit lower resistance and also higher sensitivity. This behavior can readily be understood by applying a simple series connection scheme consisting of the layers and contact resistances.

The results suggest the possibility of tuning the device performance by optimizing the geometry, at least within a certain range of parameters.



Fig. 3. Typical quantities accessible from the simulations: The device resistance (a) and the expected sensitivity (b). Fixed parameters used: electrode spacing 500 nm, specific resistivity $10^9 \ \Omega \ cm$.

Testing platform

In the outlook, the electrical response of our metal oxide thin films to different hydrogen concentrations will be measured using a twochannel (sensing and reference) sensor design. To this end, a customized gas sensor testing system will be used for the parallel and automatic data gathering of resistance variations of the sensor chips. The system has three main components: the gas handling system, the gas sensor testing chamber, and the PC and control software. The gas handling system consists of two mass flow controllers (Bronkhorst) calibrated for H₂ and air with delivery flows as low as 250 ml/min. The H₂ concentration can be varied automatically and sequentially via the control software (Demcon Convergence). The gas sensing chamber consists of 4 chambers with DIL24 quick release adapters for connecting the sensors chips to the PCB electronics. The applied voltage can be varied between 100 mV

and 10V. The electric current is recorded automatically and sequentially over time via the control software, allowing the fast and serial gathering of a high data volume at different conditions and/or materials combinations.

Conclusions

The current article presents the first steps in the rational design of a CeOx-based, miniaturized resistive sensor for H₂ detection. It is shown that ceria thin films deposited by ALD homogeneously cover complex 3D substrate geometries, increasing the effective surface of the active material and, thus, potentially enhancing the sensor response. Furthermore, the thickness of the deposited oxide can be controlled on the atomic level, leading to changes in its redox state, which can be used to tailor the ceria physicochemical properties that will determine the sensor selectivity and operational conditions. The simulation-based optimization of the electrode geometry enabled us to select the substrates with the smallest possible size and distance between the interdigitated metal fingers, providing the most efficient changes in conductivity.

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