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Characterization and gas-sensing behavior of an iron oxide thin film prepared by atomic layer deposition

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Abstract

In this work we investigate an iron oxide thin film grown with atomic layer deposition for a gas sensor application. The objective is to characterize the structural, chemical, and electrical properties of the film, and to demonstrate its gas-sensitivity. The obtained scanning electron microscopy and atomic force microscopy results indicate that the film has a granular structure and that it has grown mainly on the glass substrate leaving the platinum electrodes uncovered. X-ray diffraction results show that iron oxide is in the α–Fe_2O_3 (hematite) phase. X-ray photoelectron spectra recorded at elevated temperature imply that the surface iron is mainly in the Fe^{3+} state and that oxygen has two chemical states: one corresponding to the lattice oxygen and the other to adsorbed oxygen species. Electric conductivity has an activation energy of 0.3–0.5 eV and almost Ohmic current–voltage dependency. When exposed to O_2 and CO, a typical n-type response is observed.

Keywords: Iron oxide; Thin film; Gas sensor; Atomic layer deposition; Atomic force microscopy

1. Introduction

Semiconductive metal oxides are widely studied in order to develop inexpensive and simple gas sensors. Their applications are typically in monitoring combustible or toxic gases, such as O_2, CO, H_2, NO_2, and CH_4. Metal oxide functions as a gas-sensitive material by changing its resistance due to exposure to oxidizing or reducing gases. Typically, the target gas affects the sensor resistance by changing the density of adsorbed oxygen and/or by changing the concentration of oxygen vacancies in the lattice [1].

The gas-sensitive material can be incorporated in the sensor as a thick film, thin film, or compressed, and possibly sintered, powder. The advantage of using a thin film is that it makes the sensor fabrication compatible with integrated circuit manufacturing processes, thus allowing miniaturization and low production costs. In addition, a thin sensing layer results typically in high sensitivity, rapid response, and low power consumption.

Besides the most popular gas-sensitive oxides, e.g. SnO_2 and ZnO_2, iron oxides, either pure or doped, have been investigated for sensor applications by several authors, and promising results have been obtained [2–19]. Iron oxide thin film gas sensors have been prepared by, e.g., radio frequency sputtering [5], evaporation [6], chemical vapor deposition [7,8], sol–gel processing [11,12,15], spray pyrolysis [13], and liquid-phase deposition [17].

In this work, we investigate an iron oxide thin film grown with atomic layer deposition (ALD) for a gas sensor application. In particular, we characterize the structural, chemical, and electrical properties of the film, and demonstrate its sensitivity to O_2 and CO taken as examples of an oxidizing and reducing target gas, respectively. In ALD the film is grown in sequential cycles consisting of self-terminating gas–solid reaction steps. This provides a straightforward thickness control and typically produces highly uniform and conformal films [20–22], allowing also convenient doping [23]. Previously, the growth of Fe_2O_3 thin films with ALD has been reported by de Ridder et al. [24], Lim et. al [25], and Lie et al. [26]. Regarding gas sensor applications, the use of ALD-grown SnO_2 thin film has been reported by Utriainen et al. [27] and Rosental et al. [28].

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2. Experimental details

The sensor sample was prepared on a 4×4 mm^2 glass substrate. Before the film deposition, platinum electrodes for resistance measurement and temperature control were evaporated on the top and bottom side of the substrate, respectively. The electrode structure for resistance measurement consisted of 22 pairs of interdigital electrodes having a width of 20 µm, length of ~2 mm, and spacing of 20 µm. The iron oxide film was grown with 5000 ALD cycles at 500 °C using $FeCl_3$ and H_2O as precursors; this metal precursor is different than previously reported for the ALD growth of iron oxide [24–26]. A high deposition temperature was chosen to avoid chlorine remnants and to ensure thermal stability of the oxide.

The crystal structure of iron oxide was characterized with XRD (X-ray diffraction) using a Philips PW1830 spectrometer with Cu Kα radiation (8.04 keV). The film morphology was investigated with AFM (atomic force microscopy) and field-emission SEM (scanning electron microscopy). The AFM images were recorded with a Digital Instruments Nanoscope III operated in ambient conditions in the dynamic mode with amplitude modulation. The SEM imaging was performed with a LEO DSM-982 Gemini microscope.

For the chemical analysis of the sensor surface, XPS (X-ray photoelectron spectroscopy) was utilized. The measurements were conducted with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic Al Kα X-rays (1486.6 eV) and an electrostatic hemispherical analyzer. The spectra were recorded with a pass energy of 55 eV and an X-ray spot size of 600 µm, which gave for the Au $4f_{7/2}$ peak a full width at half maximum of 0.95 eV. The binding energy step size was 0.05 eV or 0.1 eV. The base pressure in the chamber was around 10^{-7} Pa.

Measuring the sensor resistance and controlling its temperature were accomplished with National Instruments Field Point modules and a LabVIEW-based user interface including a proportional-integral-derivative control for the sensor temperature. The sampling period was 1.5 s. The bias voltage source was connected to provide a constant voltage of 2.0 V over the sensor, irrespective of the sensor resistance.

For gas exposure experiments, the sensor sample was mounted in a stainless steel chamber which was pumped with a turbomolecular pump; the base pressure was 10^{-5} Pa. Using a vacuum chamber allowed well-defined gas exposures in a wide pressure range of 10^{-5}–1 Pa. Manual leak valves were used for gas dosing and the pressure was measured with Pirani and cold cathode gauges (Pfeiffer PKR 251). Gases used in the exposures were O_2 (99.999%) and CO (99.997%) (AGA).

3. Results and discussion

3.1. Characterization

Fig. 1 shows SEM images of the iron oxide film and an edge of a platinum electrode. AFM images of the film are presented in Fig. 2 and a typical section line in Fig. 3. It is observed that the film consists of various shapes of agglomerates whose lateral diameter varies typically between 100 and 400 nm and height between 50 and 200 nm. A profilometer result for the film thickness was about 100 nm. Although films grown with ALD are usually uniform and conformal, formation of oxide particles, e.g. ZrO_2 and TiO_2, has been reported when using chloride reactants with oxide substrates [29–31]. Increasing the growth temperature has been observed to enhance the particle formation [29–32]. While undesired for typical ALD applications, e.g. microelectronic devices, granular film structure is generally advantageous in gas sensors due to increased surface area which improves the sensitivity.

Figs. 1 and 3 indicate also that the film has grown mainly on the glass substrate leaving the platinum electrodes mostly uncovered; only separate grains of iron oxide could be detected on the electrodes (not shown). The absence of iron oxide on the electrodes was confirmed with XPS by monitoring the Fe 2p intensity while moving the X-ray spot (150 µm) from the substrate onto the electrode. In ALD with a chloride precursor and oxide substrate, the chloride precursor is considered to react primarily with surface –OH groups [31]. Thus, the observed selective growth could be attributed to the obvious difference in the density of –OH groups between the SiO_2 substrate and the platinum electrode. The catalytic nature of typical electrode

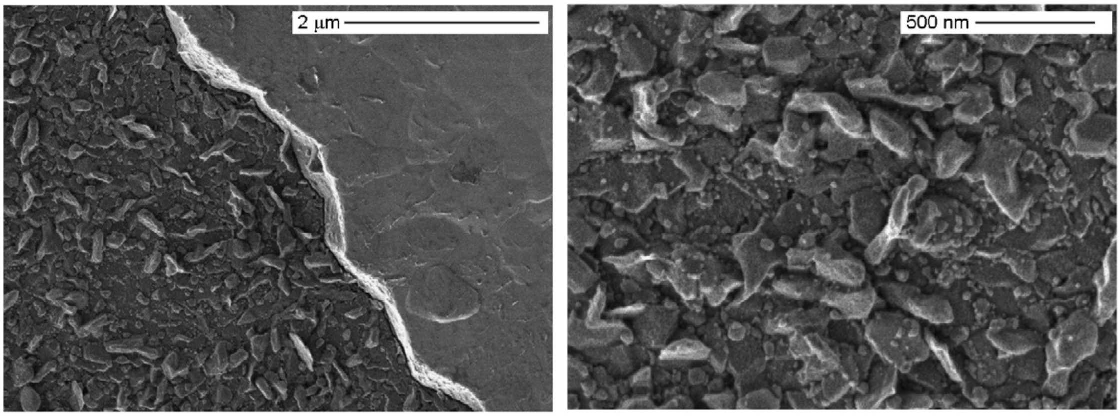

Fig. 1. SEM micrographs of the sensor surface. An edge of a platinum electrode is seen in the left-hand image.