Sensors and Actuators B 215 (2015) 525–535

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Indium-tin-oxide single-nanowire gas sensor fabricated via laser writing and subsequent etching

Maziar Afshar[a,*], Elisabeth M. Preiß[a], Tilman Sauerwald[b], Marius Rodner[b], Dara Feili[a], Martin Straub[c], Karsten König[c], Andreas Schütze[b], Helmut Seidel[a]

[a] Lab for Micromechanics, Microfluidics, and Microactuators, Saarland University, Saarbrücken, D-66123 Germany
[b] Lab for Measurement Technology, Saarland University, Saarbrücken, D-66123 Germany
[c] Lab for Biophotonics and Laser Technology, Saarland University, Saarbrücken, D-66123 Germany

ARTICLE INFO

Article history:
Received 11 September 2014
Received in revised form 11 March 2015
Accepted 30 March 2015
Available online 6 April 2015

Keywords:
Indium tin oxide
Femtosecond laser
Nanowires
Gas sensor
Self-heating

ABSTRACT

We report on the design and nanofabrication of a single nanowire (NW) indium-tin-oxide (ITO) gas sensor and on test results obtained with an oxidizing and a reducing gas. As a novel fabrication approach, direct laser writing and a subsequent etching process on sputtered ITO thin-film layers is applied. For this technique a near-infrared Ti:sapphire laser with sub-15 fs pulses and a repetition rate of 85 MHz is used. NWs for gas sensors are realized in two versions with a thickness of 125 ± 25 nm; one with 350 nm in width and 90 μm in length the other with 700 nm in width and 200 μm in length. The sensors are exposed to nitrogen dioxide (NO_2) in synthetic air with concentrations from 1 ppm to 50 ppm showing a significant change in resistance (up to 15.8%), whereas the reaction to 2000 ppm carbon monoxide (CO) turns out to be negligible (0.05%). At ambient temperature, the sensor exhibits integrating dosimeter-like behavior with relaxation times of more than 20 h. By self-heating, the NW can be reset to its initial condition, thus enabling a new dosimeter run at room-temperature. When the sensors are operated in self-heating mode, a conventional behavior is observed, enabling the detection of NO_2 concentrations down to about 1 ppm at a stationary temperature below 200 °C.

1. Introduction

Recently, micro- and nanostructured resistive gas sensors have attracted extensive interest due to their distinctive physical properties, featuring a fast response and reduced power consumption. The behavior of individual or networked single crystalline metal oxide NWs used as gas sensors has been described in previous studies [1–5]. Such sensors show promising results because of their high surface to volume ratio, a deep depletion layer in comparison to the transversal dimensions of the NW, as well as extremely low power consumption. While the sensor response of nanocrystalline thin film sensors is noticeably higher than that of single crystalline NW sensors, the detection efficiency of the latter is significantly higher. In case of SnO_2 a thirtyfold increase was reported by Bruneta et al. [6].

In single crystalline NWs, a regenerating self-heating effect can be obtained with very low energy consumption in the μW range. That makes such sensors very suitable for portable devices in contrast to their counterparts made of nanocrystalline thin films. But the fabrication is still a challenge on the way to mass-production. The self-heating effect in polycrystalline thin films can decrease the stability of a device because of grain growth [5].

The gas sensitivity is explained by a change of the band bending on the surface of the metal oxides caused by adsorption of gas molecules [7]. This band bending changes the width of the depletion layer and consequently the resistance of the sensor element.

As described by Chen et al. [3], there are two fundamentally different approaches for NW fabrication: the top-down and the bottom-up method. Most NWs described so far in the literature are based on the bottom-up concept, where many single crystalline NWs are generated in an unorganized or self-organizing configuration. This is mostly achieved by chemical vapor deposition (CVD) [3], in some cases also by electrodeposition [8]. In order to obtain a single NW for sensor applications, electron beam lithography (EBL) and/or focused ion beam (FIB) techniques are often used to select and contact a single crystalline nanostructure from randomly grown NWs [1–4,7,8]. These bottom-up approaches yield a high crystal quality but are not applicable for mass production. In contrast to these previous works, we are using a top-down approach, where a single NW with well-defined position and geometry is

* Corresponding author. Tel.: +49 681 302 4182; fax: +49 681 302 4699.
E-mail address: m.afshar@lmm.uni-saarland.de (M. Afshar).

http://dx.doi.org/10.1016/j.snb.2015.03.067
0925-4005/

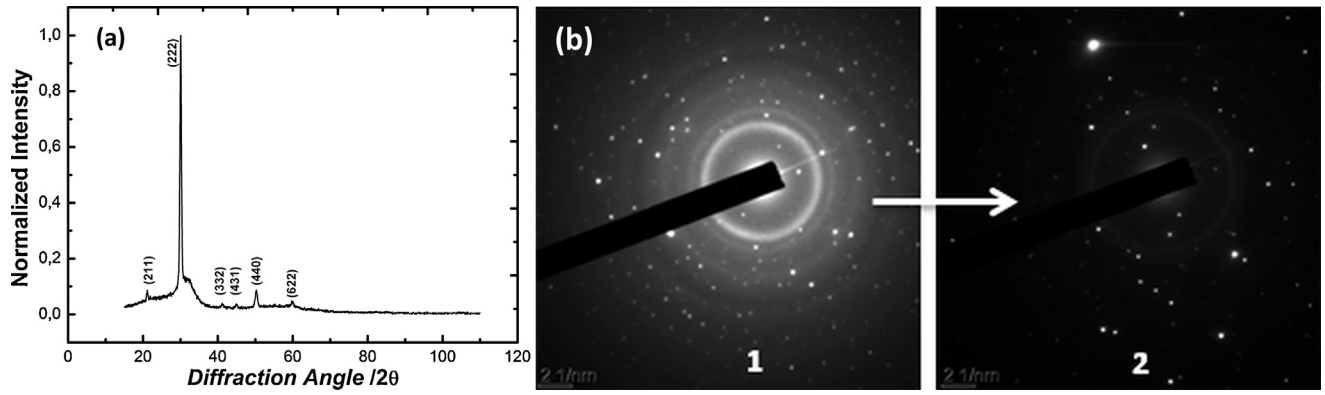

Fig. 1. (a) The X-ray diffraction spectrum of the ITO layer exhibits a strong peak from (2 2 2) planes with a slight amorphous background. It was reactively sputtered in an O_2/Ar atmosphere with an oxygen flow ratio of 3.3% out of 60 sccm total flow; (b) SAED pattern of ITO film outside (1) and inside (2) the laser-illuminated area. Laser exposure improves the crystallinity, and the amorphous background disappears.

nanofabricated directly by employing a femtosecond laser beam [9–11] in combination with a subsequent etch step.

In this way, we can generate polycrystalline ITO single NWs with lateral dimensions in the range from 60 nm up to about 1 μm [9–11]. Due to high writing speeds in the range of mm/s this method is applicable for mass production.

ITO in a typical composition is a transparent conducting oxide with a wide optical band gap and a highly degenerate electrical conductivity. It has numerous applications in display technologies, in organic light emitting diodes (OLEDs) and in photovoltaics. ITO can be considered as doped In_2O_3, which is a very common material for gas detection [12]. ITO is being commercially used in thin film sensors for the detection of oxidizing gases such as NO_2 and ozone [13]. In this article, we report on the fabrication technology of ITO polycrystalline NW gas sensors and on their sensor performance with and without self-heating effect.

The gas sensing interactions of metal oxide semiconductors at low temperatures can be more selective than sensing interactions on heated layers due to the presence of adsorbed humidity layers when gas interacts with absorbed water e.g. in terms of an acid base reaction [14]. Above 200 °C some complex chemical reactions determine the sensor behavior; poisoning of the surface and even an oxygen disequilibrium in subsurface regions takes place at temperatures above 400 °C [15]. Generally, the measurements shown in this article are performed in the range of low temperatures, up to about 200 °C.

2. Experimental

2.1. ITO film preparation

Polycrystalline ITO films with a thickness of 125 ± 25 nm were deposited on 150 μm thick glass substrates by reactive magnetron DC-sputtering (*von Ardenne LS 730S*). A compound 4-in. indium-tin (90:10) target was used in an Ar/O_2 plasma. The deposition was optimized with respect to crystallographic structure and opto-electrical properties of the films, which strongly depend on the oxygen content and on sputtering conditions. Our studies were performed with samples, which were sputtered at a chamber pressure of 0.003 mbar with an oxygen flow rate of 2 sccm corresponding to 3.3% of the total Ar/O_2 flow rate of 60 sccm. Such conditions yield layers with high electrical conductivity, allowing for a metallic contact to the pads (see Section 5).

2.2. ITO film characterization

The crystallinity of the films was analyzed by grazing incidence X-ray diffractometry (GIXRD), which showed a strong peak from (2 2 2) crystal planes (Fig. 1a). Atomic force microscopy (AFM) was used to examine the roughness of the surface (*Veeco Image 3100*). Scanning electron microscopy (SEM) was used to characterize the fabrication results on the nanometer scale.

The optical characterization of ITO films was performed by using transmission/reflection UV–vis spectroscopy (*Cary 5000 spectrometer*, *VARIAN*). Varying the oxygen flow at constant chamber pressure resulted in minor changes of the absorption edge, but single photon absorption at the laser wavelengths remains negligible [9]. Due to a very high intensity of the laser beam with a peak power in the terawatt range, we are dealing with nonlinear absorption processes in the material.

The film conductivity was examined by four-point probe measurements. ITO films sputtered at 100 W exhibited metal-like electrical conductivities (Table 1). The temperature coefficient of resistivity (TCR) α in air is positive in the measurement range of 0–90 °C (Table 1). The charge carrier density in the ITO layers was determined by Hall measurements using a van der Pauw method, yielding a value of 5.2×10^{20} cm^{-3} in a 190 nm thick ITO layer with a mobility of 8.5 cm^2 V^{-1} s^{-1}. This macroscopic effective mobility value is an average over charge densities in amorphous boundary layers and single crystal grains and is one order of magnitude below the mobility in single crystal grains. The reduction of the mobility is caused by traps and scattering centers both in the oxygen-rich and tin-rich amorphous grain boundaries [16]. This density value was used to calculate the thickness of the skin effect.

2.3. Laser processing

The sputter-deposited film was modified by using a compact optical setup (Fig. 2). The laser beam of a broadband mode-locked Ti:sapphire laser (*Integral Pro 400, FemtoLasers*) was fed into an inverted microscope (*Zeiss AxioObserver.D1*) with a galvoscan module (Jenlab GmbH), which focuses the beam into the sample through an oil immersion objective (*Zeiss EC Plan Neofluar 40×*, NA = 1.3) mounted on a piezo-actuator to adjust the focal plane vertically with nanometer precision. The laser is operated at a center wavelength of 800 nm (bandwidth 120 nm) with a repetition

Table 1
Properties of the sputtered ITO thin film. The surface roughness R_{rms} was obtained from AFM measurements. The electrical resistivity (ρ) and temperature coefficient (α) result from electrical measurements. The film thickness (d) was determined by SEM images of focused ion beam sections.

O_2 [%]	R_{rms} [nm]	ρ [10^{-4} Ω cm]	α [10^{-3} K^{-1}]	d [nm]
3.3	0.516	4.37	1	100