Scalable gas sensors fabrication to integrate metal oxide nanoparticles with well-defined shape and size

Haitao Gao[a], He Jia[b], Benedikt Bierer[a], Jürgen Wöllenstein[a,c], Yan Lu[b], Stefan Palzer[a,*]

[a] Laboratory for Gas Sensors, Department of Microsystems Engineering - IMTEK, University of Freiburg, Freiburg, Germany
[b] Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany
[c] Fraunhofer Institute for Physical Measurement Techniques (IPM), Freiburg, Germany

ABSTRACT

In this contribution, we propose and demonstrate a scalable and reproducible process to fabricate nano-sized functional particles and integrate them in microelectromechanical systems. We use a wet-chemistry approach for nanoparticle synthesis in combination with inkjet printing as a production process for metal oxide based gas sensors. This method enables control over size and shape of the nanoparticles as well as an ordered and reproducible deposition of a monolayer of particles onto arbitrary microstructures. Here we present results obtained using copper oxide nanoparticles as well as their synthesis and material characterization. A total of 14 layers has been produced and the baseline resistivity as well as the gas sensitive response towards oxygen, humidity and nitrogen dioxide of each layer has been determined.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Metal oxide based gas sensors are popular with sensor manufacturers because they can be fabricated at low-cost and feature a long lifetime. The basic principles governing the metal oxide layer's reaction towards oxidizing and reducing trace gases have been described decades ago [1–3] and theoretical models now take into account many influencing parameters such as crystallite size, grain boundary effects, surface chemistry, and the Schottky contact to read out electrodes [4–6]. However, the use of this type of chemical sensor in many demanding measurement scenarios is hindered by their lack of selectivity and the difficulty to produce gas sensitive layers with reproducible performance. To this end, the rise of nanotechnology from the 1990's onwards has opened up new avenues to control these parameters and achieve improvements in most areas of metal oxide based gas sensing. For example, single crystalline quasi 1D metal oxide structures offer high surface-to-volume ratios and consequently, the response towards trace gases is large [7–9].

New materials with tailor made capabilities to increase the sensitivity and selectivity are intended to open up new application areas. Still, for low-cost fabrication the scalable interfacing with microelectromechanical systems (MEMS) devices remains one key

challenge. Among the most promising routes for integration of nano-sized metal oxide structures into MEMS are the directed growth of nanowires on a MEMS structure [10], as well as electrospun nanowires [11], nanoscale spacer lithography [12], and using template structures to obtain well defined arrangements [13]. Scalable incorporation of ZnO nano-tetrapods onto micromachined, so-called hotplates [42,43] has been shown recently [14]. Furthermore, colloidal dispersions of nano-sized metal oxide particles appear to offer a good compromise in terms of controlling particle size and shape and scalability, while at the same time wet-chemistry approaches allow for precise incorporation of catalysts. In the past n-type semiconducting ZnO [15,16] and SnO_2 [17] − based, so called quantum dots have been deposited onto electrode structures using spin-coating or dropcasting. Work on p-type semiconducting, gas sensitive materials is less pronounced, even though e.g. CuO features interesting properties for selective trace gas detection [18–22,44] albeit at generally lower sensitivities [23]. Past work on nanostructured, tailor made CuO/Cu_2O layers included production of gas sensitive layers via the sol-gel method [24], entangled 1D nano-architectures [25], hierarchical hollow Cu_2O [26], nanowire growth by thermal oxidation [27] and nearly monodisperse Cu_2O/CuO spheres deposited via dip-coating [28].

In this contribution we present an approach incorporating p-type semiconducting CuO nanospheres that have been produced via a facile precipitation reaction, feature a narrow size distribution, and well controlled crystallite size on a low-power consuming

* Corresponding author.
E-mail address: stefan.palzer@imtek.uni-freiburg.de (S. Palzer).

MEMS structure using an inkjet printing processes. The use of this deposition techniques gives access to a high level of control in terms of positioning, distribution, and number of deposited nanoparticles. The aim is to provide means for an improvement towards a well-controlled, tailor-made gas sensitive layer morphology and composition using scalable, industry-ready techniques. Because of the narrow size distribution and the resulting possibility of producing a self-assembled, hexagonal packaging of one layer of CuO particles we investigate possible improvements with regard to the reproducibility of both the baseline and the response towards test gases.

2. Experimental

In a first step we prepare Cu_2O nano-particles according to our previously described synthesis method [29]. Therefore, 0.4832 g trihydrated copper nitrate $Cu(NO_3)_2 \bullet 3H_2O$ is dissolved in 40 ml water (H_2O) and then kept stirring for about 30 min at 250 rpm. Meanwhile, 0.4 g polyvinylpyrrolidone (PVP, average MW = 55,000) is dissolved in 60 ml water. After complete dissolution the PVP solution is added dropwise to the $Cu(NO_3)_2$ solution and the reaction mixture is stirred for 2 h. Then, 90.6 μl of hydrazine (N_2H_4) solution (35% N_2H_4 in water) is added to the reaction mixture drop-wisely. The color of the solution changes into orange immediately after the introduction of N_2H_4, which indicates the production of cuprous oxide (Cu_2O) nanoparticles. The resulting solution is kept stirring for 20 min at room temperature and then washed with H_2O and ethanol (EtOH) several times by centrifugation and redispersion (Multifuge 3 SR, Heraeus: 900g, 45 min, 21 °C). In a final step the Cu_2O nanoparticles are redispersed in 6 ml EtOH and stowed away in the dark until further use.

After synthesis the particles are characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD) and dynamic light scattering (DLS) to confirm particle size and shape, size distribution and composition. The XRD peak width is analysed using the Debye-Scherrer equation to infer the crystallite size [30].

For gas sensitive characterization of the nanoparticles we deposit them onto so-called hotplate structures [31] that have been optimized for the employed DIMATIX − DMP2831 inkjet printing system.[1] Here we use a design that features a single heater and two interdigitated electrode (IDE) structures with areas of (280 × 135) μm^2 with 7 pairs of electrodes and (220 × 115) μm^2 with 6 pairs of electrodes, respectively. The spacing between two electrodes as well as the electrode width are 5 μm and Fig. 1 depicts a schematic drawing as well as an optical microscope image of a completely processed device. We have performed temperature calibration of the chip design using thermally sensitive inks as described in [31]. A phase transition heralds a well-defined temperature of the hotplate surface and by simultaneously recording the resistivity of the heater we establish the relation between the hotplate temperature and the heater resistivity. In the experiments, we then control the heating current to attain the desired heater resistivity, i.e. the hotplate temperature, as described in [32]. The low thermal mass allows for fast temperature modulation and low energy consumption.

To deposit the ink, the print head cartridge is filled with 3 ml of the dispersion and a voltage of 25 V is applied to the piezoelectric nozzle of the inkjet printer to release a drop. To produce the gas sensitive layer used in the experiments here, 4 × 4 dots with a set spacing of 15 μm arranged in a quadratic shape are deposited twice onto the interdigitated electrode structures of each chip. Because of the surface tension and the small spacing between the individual

dots, the ink forms a single, almost round ink dot with about 60 μm diameter. Apart from that and in order to demonstrate how the inkjet process may be used to control the deposited thickness, we have produced three differently thick layers made up of one, two and four depositions of the 4 × 4 array, respectively.

This technique offers a convenient way to quickly and repeatable deposit well-defined amounts of the Cu_2O nanospheres and read-out the electrical resistivity using interdigitated electrodes. At atmospheric pressure (1013.25 mbar) and in synthetic air, i.e. at an oxygen content of 20%, Cu_2O is not stable at temperatures below 800 °C [33]. This allows for quickly converting the Cu_2O particles to CuO by heating up the sensor chip to 400 °C for 1 h, thus providing a route to use both materials derived from the same synthesis method. This step also removes the polymeric surfactant PVP. In the work presented here we use CuO and we perform gas sensitive characterizations of 7 equally processed chips using our apparatus to characterize gas sensor response [29], which yields results for a total of 14 layers. The layers have been exposed to varying levels of oxygen (0–50%), humidity (0–40%) and nitrogen dioxide (0–20 ppm) at 150 °C using synthetic air (80% nitrogen (N_2)/20% oxygen (O_2)) as carrier gas.

To analyse the data we correct for the drifting baseline via a third-order polynomial baseline fit. We use the sensor response $A(c_{Gas})$ to the trace gas concentration c_{Gas} to evaluate the layer's behaviour upon gas exposure and define it such that $A(c_{Gas}) \geq 1$, i.e. $A_{ox}(c_{Gas}) = R_0/R_G(c_{Gas})$ and $A_{red}(c_{Gas}) = R_G(c_{Gas})/R_0$ with R_0 the baseline resistivity and R_G the resistivity upon exposure to the test gas. To determine the value of R_G we use the value for infinitely long exposure times. The error of each measurement point is the standard deviation σ of the values obtained from the 14 layers. The sensor response towards the test gases is analysed using the Cliffort-Tuma model where possible, which describes the ratio of the gas sensitive layer's resistivity ($R(c_{Gas})$) upon exposure to a gas concentration c_x to the baseline resistivity R_0 using a power law:

$$R(c_x) = R_0(1 + K_x c_x)^{\pm \beta(T)} \tag{1}$$

with the temperature-dependent power law exponent β(T) and the sensitivity coefficient K_x. The gas sensitive plots are depicted using a log-log scale, such as to derive β from the slope of the graph.

3. Results & discussion

3.1. Particle characterization

Fig. 2(a) shows the XRD analysis of the particles after synthesis, which confirms the fabrication of pure Cu_2O particles with a crystallite size of 9.7 nm. The TEM images in Fig. 2(b, c) confirm this value and reveal the porous structure of the spheres. The total particle size is determined by the interaction time in presence of hydrazine, in this case 20 min. During this time, after the 10 nm crystallites are formed, they agglomerate due to Ostwald ripening to form spherical particles of growing size. This process has been described and demonstrated in [34] and here it gives us access to tailoring the size of the spherical Cu_2O particles.

The size distribution measurement using dynamic light scattering (DLS) reveals a polydispersity index (PDI) of 0.155 at a mean particle diameter of 306 nm with the surfactant polyvinylpyrrolidone (PVP) still present. The PDI is a measure of homogeneity of a size distribution and takes on the value of 0 for a monodisperse distribution and increases for increasing polydispersity. The diameter value is slightly overestimated due to the remaining PVP shell of the spheres in the dispersion.

In Fig. 3 scanning electron microscope images of Cu_2O layers with different thickness are shown. They result from printing the functional ink onto the same position for one, four, and eight times,

---