Ink-Jet printed ZnO Nanoparticles Thin Film for Sensing Applications

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ABSTRACT

By using chemical vapor synthesis, highly crystalline, less aggregated and narrow-sized ZnO nanoparticles can be obtained in high quantities. For the formation of conductive zinc oxide nanoparticle thin films, stable aqueous dispersions of ZnO nanoparticles are successfully prepared with a new polymeric stabilizer. Low porosity layers of ZnO nanoparticles with thicknesses between 100-250 nm have been fabricated on different substrates.

Ink-jet printed thin films on interdigital capacitors are investigated for electrical characterization. The measurements under ambient conditions show an increase in conductivity with increasing temperature. The resistance in hydrogen decreases by a factor of five compared to measurements performed under ambient conditions even at room temperature.

Keywords: ink-jet printing, sensing, ZnO, impedance spectroscopy, thin film

1 INTRODUCTION

The increasing demand for transparent conducting materials as they are used for instance in touch-panel controls and flat panel displays [1,2] requires alternative materials and production technologies due to the rising costs and increasing shortage of indium tin oxide (ITO). Besides other materials, ZnO is an attractive candidate to replace the commonly used ITO due to its properties and availability. A comparison between ZnO and ITO concerning the optical and electrical properties has already shown the abilities of zinc oxide and its promising features [3-5].

While most of the conductive layers are produced by Chemical Vapor Deposition (CVD), Physical Vapor deposition (PVD) and sputtering, the amount of material required to synthesize functional layer and structures can be significantly decreased by using printing technologies like roll-to-roll printing and inkjet printing. Ink jet printing is also an interesting feature for the production of diodes or organic electrodes [6,7]. In comparison to the methods mentioned above, printing technologies usually do not require inert conditions or high vacuum systems. However, stable dispersions of the active material are needed meeting the requirements with respect to stability and printability

In this proceeding it is shown that we are able to synthesize stable dispersions from ZnO nanoparticles that can be used to prepare functional, conductive and sensing devices by using a simple ink-jet printing technology. In contrast to established technologies used for the formation of functional devices, no annealing or post-processing is required.

2 EXPERIMENTAL DETAIL

ZnO nanoparticles are synthesized by chemical vapor synthesis (CVS) in a hot-wall reactor. A gaseous mixture of diethylzinc and oxygen passes a wall-heated tube kept at a temperature of 1073 K. Decomposition and oxidation of the precursor leads to the formation of zinc oxide, CO_2 and water vapor. Downstream the reaction zone the as-synthesized particles are separated from the gas by means of a thermophoretic sampler.

The freshly prepared ZnO nanoparticles have a spherical shape. The x-ray diffraction measurements (XRD) analyzed with Rietveld refinement [6] reveal crystalline zinc oxide nanoparticles with the wurtzite structure of ZnO. The mean crystallite size calculated from XRD data using the Scherrer equation is about 20 nm in diameter.

Stable dispersions of as-prepared zinc oxide nanoparticles were prepared by sonication of an aqueous mixture consisting of 10 wt% of a polymeric stabilizer and 10 wt% of the ZnO nanoparticles. The dispersion is stable for at least a couple of months.

Interdigital capacitors with a structural width of about 400 nm and a contact spacing of about 500 nm were synthesized by using electron beam lithography. The interdigital structures were written on a silicon substrate covered with an insulating oxide shell. The structures consist of two opposite gold pads with gold fingers arranged in between (see figure 1).

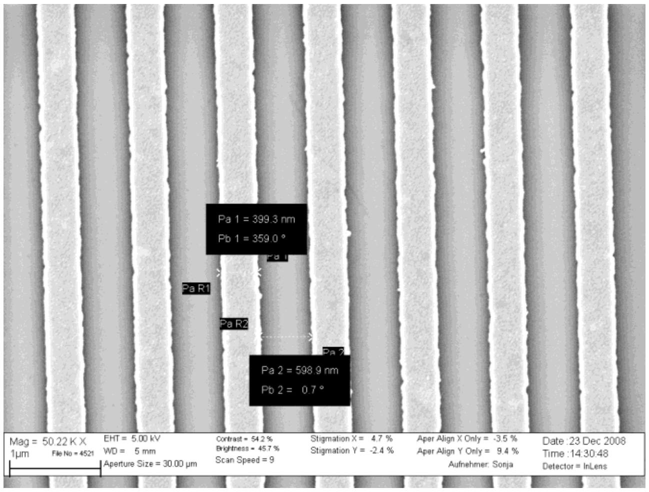

Figure 1: SEM picture of an interdigital capacitor with gold contacts prepared by means of electron beam lithography.

For the electrical characterization of zinc oxide layer, dispersions of ZnO nanoparticles were printed on top of the interdigital capacitors. To ensure a good wetting, the produced interdigital structures were shortly exposed to piranha solution. A Dimatix 2800 ink-jet printer was used to produce the thin films.

For the subsequent electrical characterization, the interdigital structures with the ink-jet printed films on top were mounted in a chip carrier and electrically connected to its contacts (see figure 2). The chip carrier was installed and connected to a gas-tight measurement cell that enables for the control of the gas atmosphere within the cell.

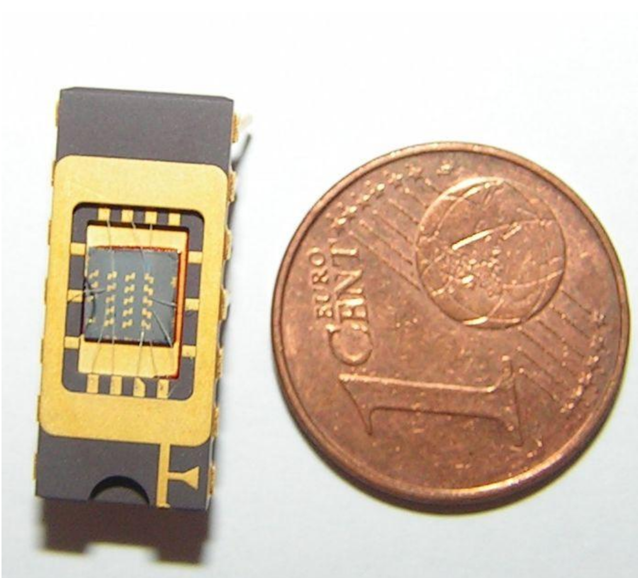

Figure 2: Array of 15 interdigital capacitors mounted in a chip carrier compared to a one cent piece.

The electrical properties of the printed films were characterized using impedance spectroscopy. The impedance was measured in the temperature range between room temperature and 473 K using an impedance spectrometer Solartron SI 1255. Data were taken in the frequency range between 10 Hz and 10 MHz with 20 frequency points per decade.

3 RESULTS AND DISCUSSION

3.1 Printing and Structural Properties

After the optimization of printing parameters like frequency, platen temperature, firing voltage and drop spacing, porous but very smooth zinc oxide films with a surface roughness which is negligible could be printed with high reproducibility. The printed layer were free of cracks and the thickness of the ink jet printed films could be varied between 100 and 250 nm.

It was observed, that the initial crystal size of about 20 nm in diameter increased up to 36 nm in diameter after printing and storing the zinc oxide films under ambient conditions. This behavior is attributed to the presence of moisture and its effect on crystal growth as described for ZnO nanoparticles from gas phase synthesis [8]. It is assumed, that this post-printing growth helps to enhance the conductivity of the thin film and to decrease the number of poorly conducting grain boundaries. Therefore, the ripening under ambient conditions may be denoted as an annealing process.

3.2 Electrical Properties

The electrical properties were measured using impedance spectroscopy. After a first measurement performed at room temperature, the sample was heated in steps of 25 K up to 473 K. After the measurements carried out in air the samples was allowed to cool down and the composition of the gas within the measurement setup was changed from air to hydrogen followed by an electrical characterization as escribed before.

As expected, the measurements in air show an increase in conductivity with increasing temperature. The Nyquist plots show typical semicircles as they are known from the electrical characterization of semiconducting materials by means of impedance spectroscopy (see figure 3).

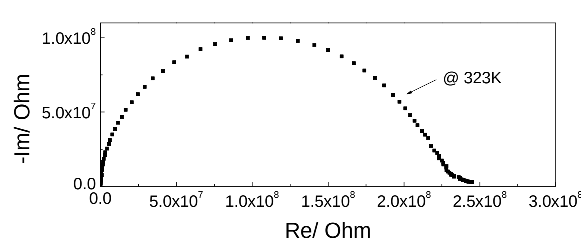

Figure 3: Nyquist plot (imaginary part of impedance vs. real part of impedance) measured at 323 K in air.

At low frequencies, almost DC-conductivity is observed (see the conglomeration of measurement points at the right side of the semicircle). The temperature-dependent conductivity taken from values in this DC-range was used to calculate the activation energy of the charge carrier transport process. The activation energy for the measurements under ambient atmosphere was calculated to be 101 meV, which can be attributed to a temperature-activated electronic conductivity.

For simple testing of the sensing properties, the sample was exposed to hydrogen atmosphere after finishing the measurements in air as described above. The conductivity in hydrogen increases by a factor of four even at room temperature compared to the measurements in air and the activation energy for the measurements in hydrogen atmosphere was calculated to 108 meV which is almost the same compared to the measurements in air.

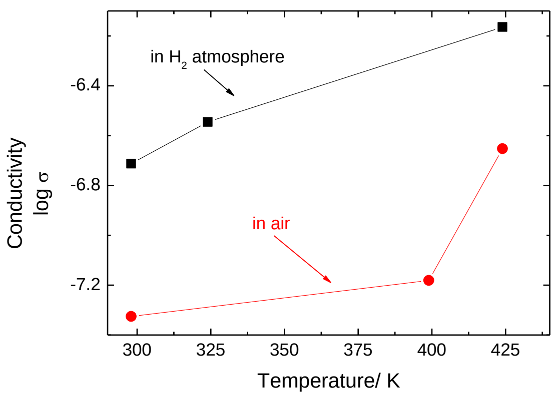

Figure 4: Conductivity as a function of temperature for the measurements in air and hydrogen atmosphere.

As a result, the increase in conductivity by exposing the ZnO nanoparticles to hydrogen atmosphere can be explained by the generation of free electrons due to the release of oxygen from the lattice under reducing conditions [9]. Therefore, by using hydrogen as environment, the concentration of charge carriers increases resulting in higher conductivity compared to the measurements in ambient atmosphere.

It is expected that the response time of our thin-film sensors is much higher than that measured for common thick film sensors. As the printing of conducting structures is an established technology, a very promising advantage of our finding is that with the materials and technology described above it must be able to fully print functional sensor devices even on highly temperature-sensitive substrates such as polymers.

SUMMARY

As a result, it has been shown that we are able to synthesize stable dispersions from ZnO nanoparticles that can be used to prepare a functional sensing device by simple ink-jet printing. In contrast to established technologies used for the formation of sensor devices, no annealing or post-processing is required.

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