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Inkjet printed In_2O_3 and In_2O_3/CNT hybrid microstructures for future gas sensing application

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Abstract:
We report on the fabrication of *In_2O_3/multiwalled carbon nanotubes* (*CNTs*) composite *microstructures* via *inkjet printing*. The active sensor materials were derived from an inkjet printed suspension of carbon nanotubes and molecular In_2O_3 metalorganic *single source precursor* onto Si, SiO_2 or alumina substrates followed by thermal conversion and gas sensing measurements. We found a good correlation of printed microstructures (e.g. tracks 100-150 µm wide) with pre-defined programmed patterns and a homogeneous distribution of CNTs in the composites. The ink-jet printed morphology is scalloped and continuous without breaks. Critical printing parameters like printing resolution or 'coffee stain effect' can be successfully controlled by changing precursor solution viscosity, substrate temperature and number of layers repeatedly printed on top of each other.

Key words: metal oxides, multiwalled carbon nanotubes, composites, microstructures, single source precursors, inkjet printing.

Introduction

Hybrid nanomaterials, which consist of polycrystalline semiconducting metal oxides (*e.g.* In_2O_3, ZnO, Ga_2O_3, CuO) and carbon nanotubes (CNTs), possess a higher conductivity than the pure metal oxides, and are promising for future gas sensing applications.[1] CNTs can provide better contacting of metal oxide grains, thus, the sensing response of a larger fraction of the semiconducting material can be obtained. Therefore, such composites can be useful towards further miniaturization of gas sensing devices without lowering their sensitivity or selectivity. A step towards miniaturization of gas sensing elements is the integration of nanoscale composites into micron-scale structures of desired geometry *via* microstructuring. In this regard, printing techniques, such as inkjet [2] or flexography are very promising. The inkjet printing of functional materials allows integrating nanoscale hybrids into microstructured gas sensors with the resolution of tens of microns, *i.e.* bridging nanotechnology and microscopic patterns. The expected advantages of such microintegrated hybrid sensing elements in comparison with pure metal oxides are *e.g.* higher activities at ambient temperatures and lower power consumption. A further advantage of inkjet printing is that it is a non-contact technique, which does not require any masks for design and repeated production of microscale patterns. This method enables one to fabricate high quality patterns on a big variety of flexible paper- or polymer-based substrates, and suits for the inexpensive production of sensor modules for microelectromechanical systems (MEMS).[3]

Experimental

Metal oxide precursor (In-oximato complex) was synthesized and purified as described elsewhere.[4] The inks were prepared in the following manner: 500 µg of CNT's (Electrovac™) were first dispersed in 20 ml DMF or 2-methoxyethanol by ultrasonication for 2 h, then centrifuged for 30 min at 3000 rpm and decanted, the latter procedure was repeated twice. A stable dark-grey CNT's dispersion was obtained. After that, 200 mg of indium oximate were dissolved in 3 ml of the CNT dispersion, and the complete ink composition was homogenized in an ultrasonic bath. Inkjet printing was performed using a Dimatix DMP 2811 printer with 16 nozzles of 20 µm size (Fujifilm Dimatix, Inc.), typically at 60 °C substrate temperature. Silicon wafers (1.5 ×

1.5 cm) and silicon slides with 230 nm thermally grown silicon dioxide (Fraunhofer IWS Dresden) were ultrasonically cleaned with acetone, isopropanol, and water (ACS-reagent, Sigma-Aldrich), and used as substrates. For prospective DC electrical measurements (gas sensor tests), inks were also printed on top of alumina substrates with Pt-electrodes on the front side and an integrated heater on the backside. The printed samples were first dried at 130 °C in the air for 2 h, and, after that, heated to 350 °C for another 2 h. Surface topography, thickness and cross-sectional views of printed samples were analyzed with a NewView 6200 optical profilometer (Zygo). SEM/EDX analysis was performed on a XL-30 FEG (Philips). Qualitative X-ray analysis (XRD) of the composites was carried out on a STOE STADI 4 4-circle-diffractometer using Cu Kα1 radiation (λ = 1.541 Å). TG/MS measurements: TG 209N1 coupled with Aelos QMS 403C (both Netzsch).

Results and discussion

Preliminary thermogravimetric studies (not shown here) revealed that conversion of the hybrid composition of In_2O_3-precursor with multiwalled CNTs (Electrovac™, diameters 100-150 nm) into the final metal oxide/CNT composite is finished at 330-350 °C. The XRD analysis of such a composite (Fig. 1) shows no carbon-related reflexes (no long-range ordering in CNTs). The In_2O_3 crystallite size (Scherrer method, (222) reflex) at 330 °C is around 27 nm depicting comparable diameters of metal oxide grains and CNTs, and, therefore, their homogeneous distribution within the composite.

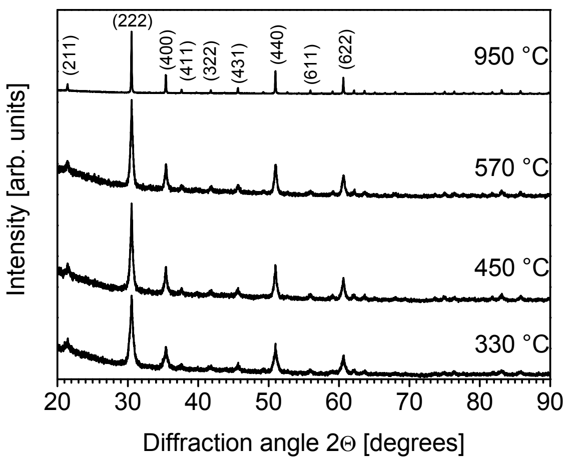

Fig. 1. XRD patterns of In_2O_3/CNT composites after every thermal conversion step according to the TGA analysis. The mass loss events at 450 and 570 °C correspond to the CNTs oxidation, however, broadened reflections demonstrate that In_2O_3 crystallites resist agglomeration at high temperatures.

The information about crystallite sizes corresponding to conversion temperatures is summarized in Table 1. Evidently, In_2O_3 crystallites maintain their nanoscopic dimensions at temperatures significantly higher than normal gas sensor operating conditions.

Tab. 1: Mean crystallite sizes of In_2O_3 according to Scherrer equation after every decomposition step.

Conversion temperature, °C	Crystallite size, nm (calculated from (222) reflex)
330	27
450	38
570	41
950	114

Inkjet printing of the molecular indium ketoacidooximate/CNT hybrid material dispersed in 2-methoxyethanol on various substrates (Fig. 2 and 3) resulted in an equidistant line pattern of 100 µm wide lines which are continuous and well separated from each other. Their width does not exceed 150 µm. A slight 'coffee stain effect' is visible (height of 0.01-0.05 µm in the middle and 0.05-0.15 µm at line borders).

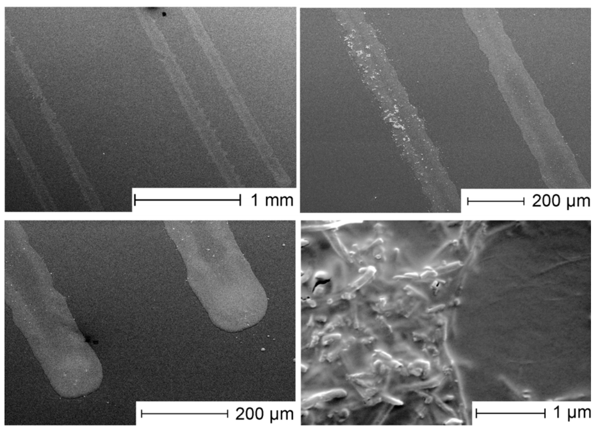

Fig. 2. A SEM image of the inkjet-printed indium precursor with CNTs on Si. The CNTs are homogeneously embedded in the printed composite. The width of observed lines is around 150 µm.

For initial sensoric measurements a discrete line pattern was also printed using solution of the pure indium ketoacidooximate molecular precursor and studied with respect to its sensoric behaviour. This printing was performed over alumina substrates with integrated Pt-electrodes for DC-measurements and Pt-heaters on the backside that allow to keep constant desired temperature during gas sensing measurements (Fig. 4).

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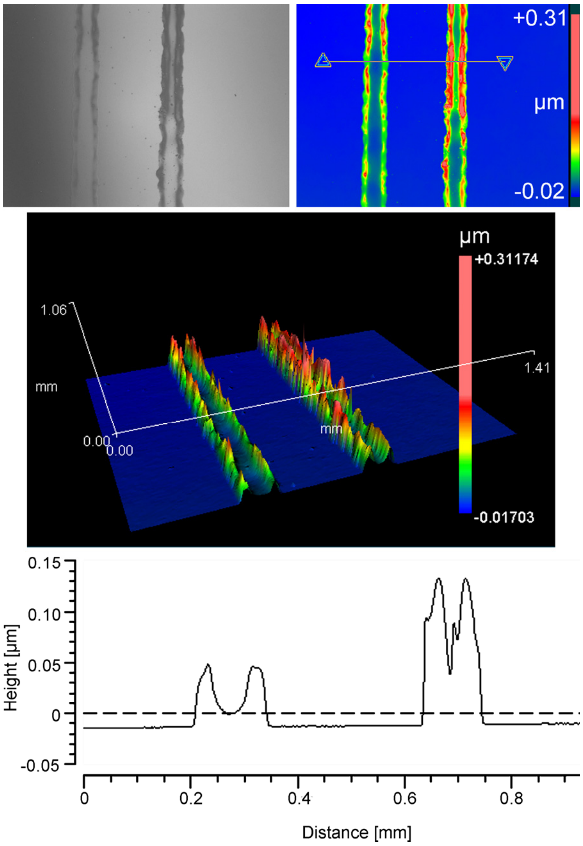

Fig. 3. Optical microscopy and 3D-images of inkjet printed tracks of the molecular indium ketoacidooximate precursor with multiwalled CNTs on Si substrate. The height profile shows the printed features which are due to the 'coffee stain effect'.

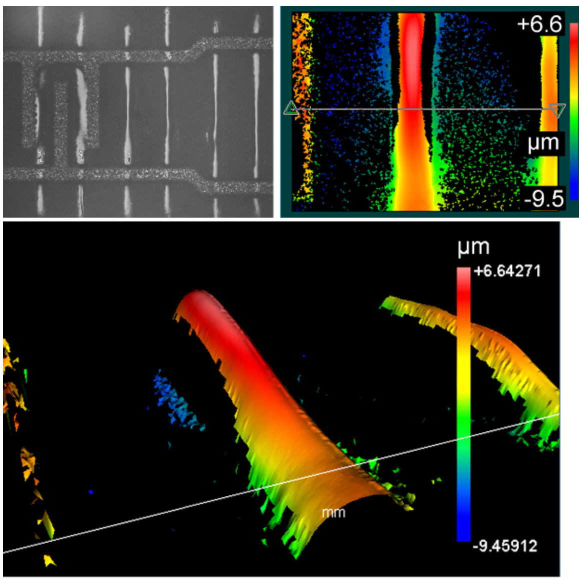

Fig. 4. Optical microscope image (above left) and 3D-visualisations of inkjet printed In_2O_3 precursor over alumina substrates with incorporated Pt-contacts for gas sensing measurements. Alumina substrate is not visible in the 3D-image due to the polycrystalline nature of the substrate and light scattering effects.

Preliminary gas sensor tests were performed with CO (10 – 100 ppm) and H_2 (500 – 5000 ppm) in N_2 atmosphere at temperatures between 200 - 400 °C and showed promising sensor performance and reversibility of the microstructured In_2O_3 materials. Figure 5 shows the measurement performed with indium oxide at 200 °C. The plot demonstrates resistance decrease upon exposure to reducing gases. The material reproducibly responds to the low concentrations of carbon monoxide, the sensitivity towards hydrogen is, however, slightly less pronounced. In the case with H_2, preliminary experiments revealed the measurement limits around 1000 ppm, since the resistance is changed only a little at higher concentrations.

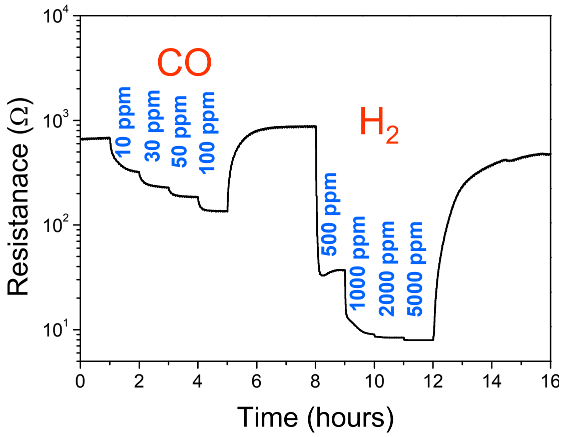

Fig. 5. DC-measurements plot reflecting the sensitivity of In_2O_3 samples towards small concentrations of reducing gases (CO and H_2).

Conclusions

To summarize, we demonstrated homogeneous metal oxide/CNTs composite preparation from metalorganic single source precursor and multiwalled CNTs. The suspension inks were compatible with various substrates, like Si, SiO_2, and alumina, and allowed good resolution of printed microstructures. Preliminary sensor tests showed good contacting of inkjet printed In_2O_3 tracks with Pt-electrodes. These results point to the conclusion that the prepared inks are very promising for production of nano-micro integrated gas sensing elements.

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