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# Layer by Layer Deposition of Colloidal $SnO_2$ Nano Particles †

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**Abstract:** The gas sensing properties of functional metal oxide layers depend on multitude parameters, including vacancy concentration, layer morphology and thickness, size and shape of the nano/microstructure, and porosity. Using colloidal tin oxide inks we demonstrate a layer by layer deposition technique to control the thickness and composition of gas sensitive layers. To do this we combine inkjet-printing with colloidal suspensions of $SnO_2$ particles to provide a scalable method to interface microelectromechanical systems (MEMS) with nano particles. The approach may pave the way towards an industry ready integration technique to incorporate gas sensitive quantum dots or hybrid nanomaterials in arbitrary sensing devices.

**Keywords:** tin oxide; colloidal dispersion; inkjet printing; nano-micro integration; MEMS

## 1. Introduction

Recently, the complete processing of a $SnO_2$-based sensor on a flexible substrate has been shown [1] along with notable advances in the control of material composition using e.g., electrospinning [2], quantum dots, and nanowires has been achieved. While intense research efforts in all of these areas are underway the use of wet-chemistry synthesized metal oxide particles in a colloidal dispersion in combination with inkjet printing offers distinct advantages because that offers a way to control most of the influencing parameter to a high degree [3]. Here we use a colloidal dispersion of $SnO_2$ nanoparticles to deposit them layer-by-layer. While intense research efforts in all of these areas are underway the use of wet-chemistry synthesized metal oxide particles in a colloidal dispersion in combination with inkjet printing offers distinct advantages because that offers a way to control most of the influencing parameter to a high degree [3]. Our latest results use a colloidal dispersion of $SnO_2$ nanoparticles to deposit them layer-by-layer.

## 2. Experimental

To demonstrate the possibility of depositing the a colloidal tin oxide ($SnO_2$) ink on arbitrary substrates we use a hotplate platform that has been tailor made for testing novel functional inks [4]. The microelectromechanical system (MEMS) features a heating structure surrounding a round interdigitated electrode area of 120 µm diameter. Both structures are achieved by sputtering 20 nm tantalum (Ta) and 200 nm platinum (Pt) on top of a device layer consisting of 1 µm silicon oxide ($SiO_2$), 4 µm silicon (Si), and 400 nm p-type Boron-doped low-stress silicon nitride (SiN) [4].

The synthesis route to obtain the $SnO_2$ colloidal ink starts with $SnCl_4 \cdot 5H_2O$ (1.5 g), which is firstly reduced to Sn by $NaBH_4$ (0.29 g) in the media *N*,*N*-dimethylformamide (60 mL) and thereafter oxidized at elevated temperature (120 °C, 20 min) to $SnO_2$ particles [5]. After removal of the impurities by careful washing using $H_2O$ and ethanol, the final solid product is dispersed in 10 mL $H_2O$. Take 2 mL from above colloid suspension and mixed with 0.01 g PVP (MW = 55,000). The zeta potential and viscosity are adjusted such that the resulting ink is compatible with the DIMATIX inkjet printing system. Each inkjet dot may be deposited with a precision of 15 µm and after evaporation of the liquid phase a single ink dot deposition results in a surface coverage well below a monolayer. Because PVP has been added as a surfactant the $SnO_2$ particles after deposition are coated with the polymer as can be seen in Figure 1. Using a thermal treatment in the presence of oxygen, the remaining polymer is burned away and this results in a layer made of pure $SnO_2$ nanoparticles. The thickness of the layer can now we controlled precisely by the number of printing repetitions. Multi-layer systems feature a high porosity and the gas response depends not only on the porosity but also on the thickness of the $SnO_2$ layer. A microscope image of a completely processed device including a single, multilayer $SnO_2$ dot is shown in Figure 2.

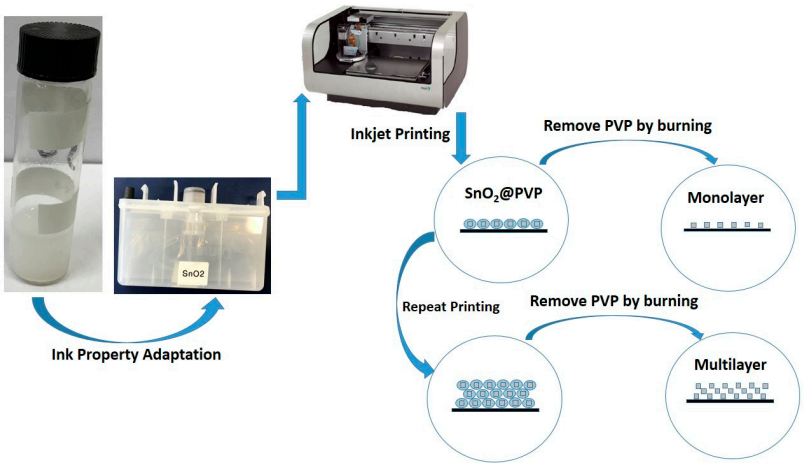



**Figure 1.** Schematic overview of the layer-by-layer production process. Using colloidal inks with low solid state content it is possible to tune the deposited layer thickness from below a monolayer to a porous multilayer system via repetitive dropping of ink dot on the same spot.

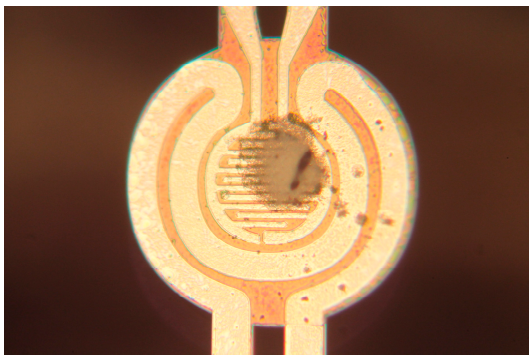
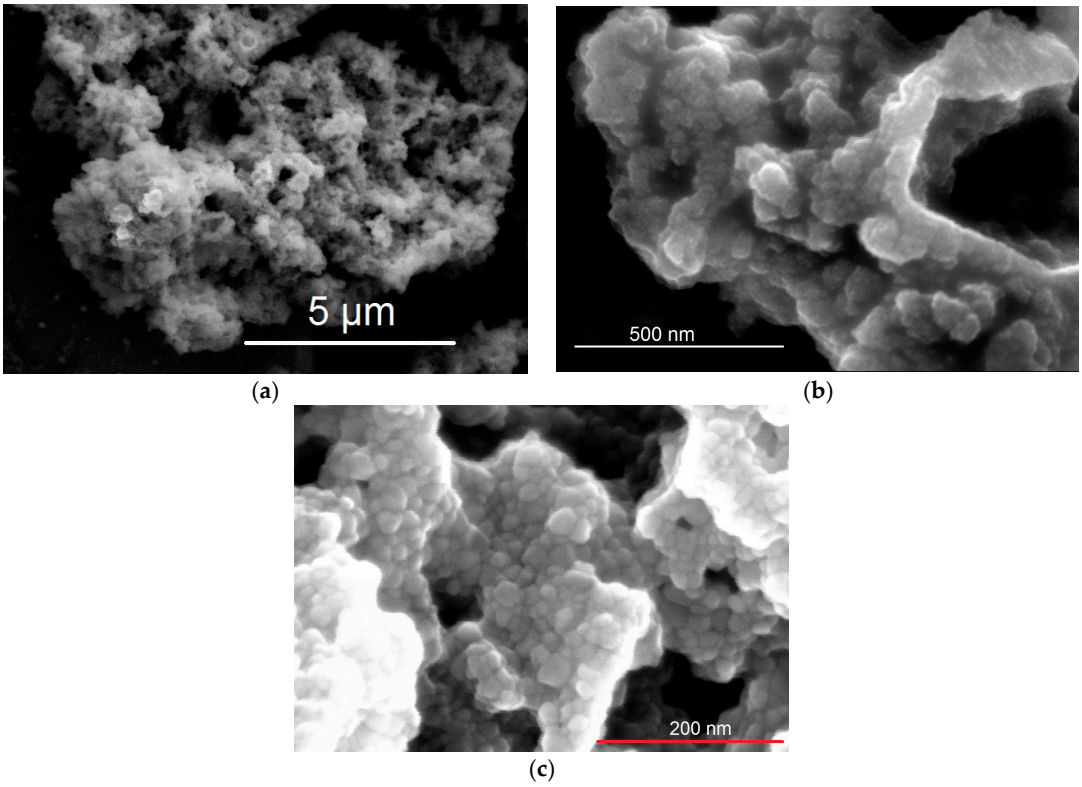


**Figure 2.** Microscopy image of a hotplate with a deposited $SnO_2$ layers after thermal treatment to burn the polymer matrix. The ink composition does need further optimization, which is evident from the satellite dots and the inhomogeneous $SnO_2$ layer thickness.

## 3. Results

In an initial characterization the $SnO_2$ colloidal ink has been investigated using a scanning electron microscope. The result is depicted in Figure 3 and shows the PVP coated and agglomerated

$SnO_2$ particles. The poor homogeneity of the distribution is due to a non-ideal zeta potential and subsequent improvement have to focus on the particle distribution after inkjet printing.




(**a**) (**b**)

(**c**)

**Figure 3.** (**a**) Scanning electron microscopy image of the $SnO_2$ polymer matrix in a 10,000 fold magnification as deposited on the hotplate structure; (**b**) A 100,000 fold magnification of the same $SnO_2$ polymer matrix; (**c**) After burning the PVP the $SnO_2$ nanoparticles sinter together during the heating process and agglomerate in clusters of several 100 nm.

During polymer burning the $SnO_2$ particles sinter together and create randomly shaped clusters of several 100 nm diameter.

**Conflicts of Interest:** The authors declare no conflict of interest.

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