

# New selective gas sensors based on printed semiconductor nanoparticles – SEGASE

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## 1 Introduction

Different kind of gas sensors have been widely used in several applications in industry, vehicle technologies, health care, household appliances and alarm systems, etc. The problems of the currently available gas sensors are their often rather expensive fabrication costs, high energy consumption, and low selectivity for detected gases. Thus there is a need for novel gas sensor technologies. Using novel sensor concept which is based on nanostructured Metal-Electrolyte-Insulator Semiconductor (MEIS) transistors, the functional properties of sensors can be improved. As sensors are produced using modern printing technologies, more effective and cheaper gas sensors can be fabricated. SEGASE is a Finnish National Technology Agency (TEKES) funded cooperation project with Oulu University (Optoelectronics and Measurement Techniques Laboratory and Microelectronics and Material Physics Laboratory), VTT, and Kurchatov Institute from Russia, and three industrial partners. In Figure 1, there is a flow chart of tasks of different partners in SEGASE project.

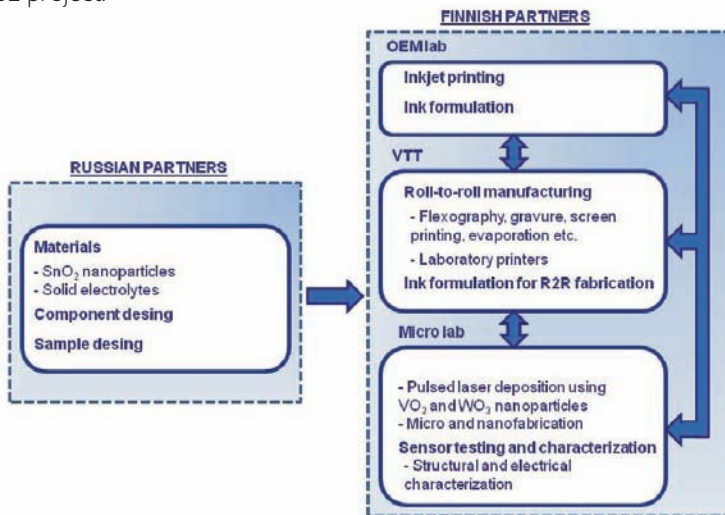


Figure 1 Tasks of different partners in SEGASE project.

## 2 Objectives of the research

The goal of this project is to research and develop new materials and fabrication methods that can be used producing highly selective, low power consumption, and cost effective gas sensors. The possibility to fabricate a sensor matrix for detecting multiple gases simultaneously is also investigated.

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### 3 Results

The proposed sensor can be considered as a transistor with the structure Metal-Electrolyte-Insulator-Semiconductor (MEIS). Gas absorption causes a shift along the voltage axis of the I-V curve of the transistor. The gas concentration can be determined based on that shift along voltage axis. Printing routes including roll-to-roll manufacturing technique will be investigated in order to lower further the manufacturing costs and to enable multi-array miniature sensors to be developed on rigid and flexible substrates. The proposed gas sensor concept is developed for following target gases:  $H_2$ ,  $CO$ ,  $NO_x$ ,  $O_2$ ,  $H_2S$ . The possibility to fabricate a sensor matrix for detecting multiple gases simultaneously is also investigated. In Figure 2, there are inkjet and gravure offset printer used for gas sensor fabrication shown.

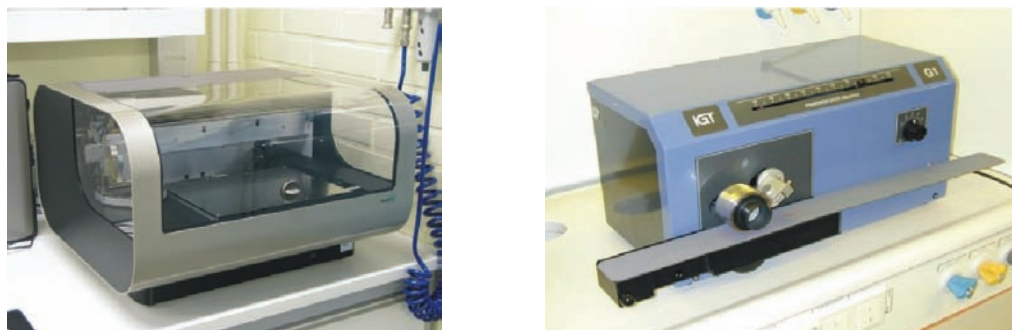


Figure 2 (a) Inkjet and (b) gravure printers.

On the other hand, tungsten oxide  $WO_3$  in its various forms is studied as an active material for gas sensing in MEIS structures. Mesoporous anodic tungsten oxide (Figure 3a) is formed by electrochemical etching of tungsten metal in aqueous NaF solutions (0.15 M NaF, 3 hours, 60 V) [1]. The porosity of the oxide can be modified by changing the experimental parameters to obtain optimal feature scale for specific application as has been demonstrated by other mesoporous oxides as well [2]. The anodized film can be cracked to sub-micrometer size particles and stripped from the substrate when submerging in water to form a colloidal dispersion.  $WO_3$ -based sensors are obtained by drop casting the dispersion between Pt-electrodes (defined on Si/SiO<sub>2</sub> chips) followed by calcination in air at 400 °C to obtain monoclinic  $WO_3$ , which is commonly known as an excellent material for gas sensing applications. The obtained resistive (Taguchi-type) gas sensor (Figure 3b) was observed to be sensitive to  $CO$ ,  $H_2$ ,  $NO$  and  $O_2$  analyte gases with the highest sensitivity to  $NO$  and  $H_2$  gases.

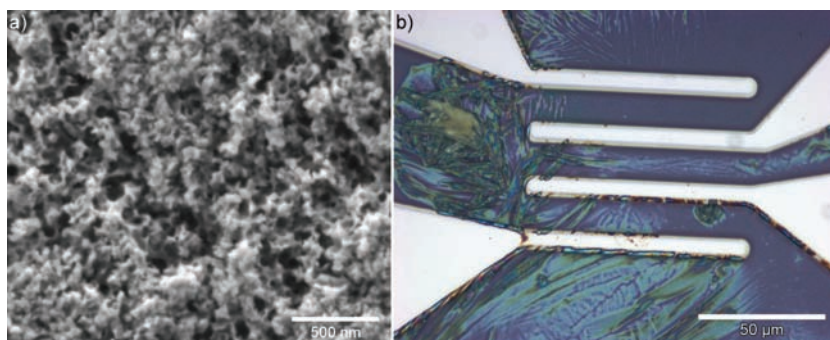
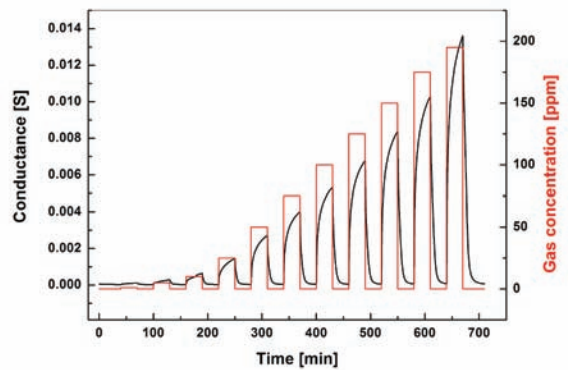
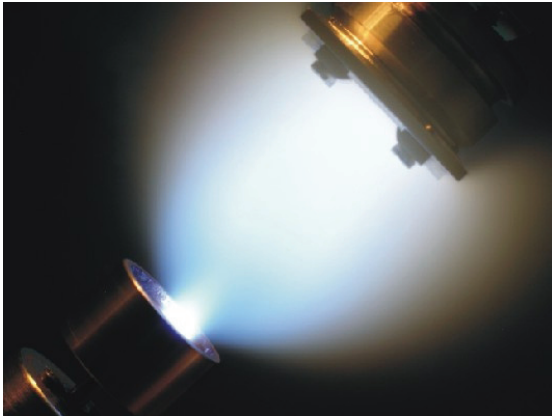


Figure 3 (a) FESEM image of anodic tungsten oxide and (b) optical micrograph of a  $WO_3$ -based sensor with a drop cast and annealed anodic tungsten oxide film on Si/SiO<sub>2</sub> (with Pt-electrodes).

Pulsed laser deposition (PLD) method seems to be promising for fabrication of  $\text{WO}_3$  nanostructures with well defined properties. Nanoparticles of electrochromic  $\text{WO}_3$  ceramics show some extremely interesting properties by having ferroelectric-like polarization when the grain size of the material is small enough, below  $\sim 10$  nm. In such a case,  $\text{WO}_3$  seems to go through a phase transformation at room temperature to  $\epsilon$ - $\text{WO}_3$  phase, which is normally stable only at lower temperatures. The phenomenon is not yet fully understood and requires a lot of basic research. However, these kinds of nanoparticles of  $\text{WO}_3$  have many potential application areas on the field of novel ferroelectric devices, nematic displays, sensitive gas sensors, etc. PLD grown as-deposited  $\text{WO}_3$  films have shown good sensitivity to, for example,  $\text{H}_2\text{S}$ .

In this work, we report some new results of the properties of PLD deposited  $\text{WO}_3$  nanostructures (Figure 4a). Optical and structural properties were investigated as function of annealing temperature by using spectrophotometry, X-ray diffraction (XRD), Raman spectroscopy, and scanning probe microscopy (SPM). The influence of post-annealing thermal heat-treatment on the formation of  $\text{WO}_3$   $\epsilon$ -phase is discussed. Gas sensitivity responses of  $\epsilon$ - $\text{WO}_3$  phase nanocrystalline sensor elements were measured for several gases including  $\text{H}_2\text{S}$  (Figure 4b),  $\text{NO}_x$  and  $\text{H}_2$ .



ppm in synthetic air measured at 200 °C of a  $\text{WO}_3$  film with  $\epsilon$ -phase deposited at room temperature and afterwards annealed at 400 °C.

#### 4 Relevance of the research

The main effort of SEGASE project is focused on finding and developing suitable low-cost manufacturing methods for MEIS transistor based gas sensors, including the first time use of inkjet printing for discovering new nanocomposites and enabling multidetection low cost sensor arrays on rigid and flexible substrates in several applications in industry, vehicle technologies, health care, household appliances, and alarm systems, etc.

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