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Pulsed Laser Deposition of Metal Oxide Nanoparticles, Agglomerates, and Nanotrees for Chemical Sensors

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Abstract

Pulsed laser deposition (PLD) was used to prepare WO_3, ZnO-modified SnO_2, and V_2O_5 nanostructures as gas sensing materials on top of commercial SGX Sensortech MEMS microheater platforms. The layers were formed of different types of nanostructures including nanoparticles, agglomerates, and nanotrees with fractal-like growth. Clear dependency between the deposition parameters, structural morphology, and gas sensing performance was found. The sensing materials were found to be sensitive to different types of gaseous species, so that WO_3 and SnO_2 had very good response up to 600 % to 50 ppm NO, and V_2O_5 up to -35 % to 20 ppm NH_3, respectively.

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1. Introduction

Today there is growing need for cheaper and more effective gas sensing solutions in order to control the quality of

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indoor and outdoor air by reducing emissions from, *e.g.* from traffic and buildings including furniture, décor and human activity. The most widely studied gas sensor components nowadays are probably metal-oxide-semiconductor (MOX) gas sensors. MOX sensors are a strong candidate for different types of gas sensing systems because of their simple operating principle, low cost, and high sensitivity. However, some drawbacks also exist, for example poor selectivity. Pulsed laser deposition (PLD) is a novel method to manufacture these types of metal oxide based gas sensing layers [1]. A great advantage of the method is the easy control of film structure by variation of the deposition parameters. Under high O_2 partial pressure in the deposition chamber during the process, nanoparticles start to form already during the expansion of the plasma from the target surface to the substrate [2]. Also, gas sensing studies with PLD coated MOX sensors manufactured on MEMS microheater platforms were performed. In this study, we show how crystal structure and structural morphology of the metal oxide layers can be controlled by PLD process parameters and how this relates to the gas sensing performance.

2. Experimental

Excimer laser operating at a wavelength of 308 nm (Lambda Physik Compex 201) with a pulse repetition rate of 5 Hz was used to deposit thin metal oxide layers on oxidized silicon substrates, and also to commercial MEMS microheater platforms. Ceramic V_2O_5, WO_3, and ZnO-modified (0.3 % of volume) SnO_2 targets were used and the laser pulse energy density was I = 1.25 J/cm^2. All the depositions were performed at room temperature. The deposition chamber was first evacuated to a base pressure of ~5x10^{-5} mbar, and then oxygen partial pressures of $p(O_2)$ = 0.08 mbar, 0.1 mbar, or 0.2 mbar were injected into the chamber. Post-annealing process in a furnace in temperature of 400 °C at room atmosphere for 1 h period was used. Crystal structure of the films was studied using grazing incidence diffraction-method (GID) of X-ray diffraction (XRD) by Bruker D8 Discover facility. Scanning electron microscopy studies for sensing layers were performed with Zeiss Sigma FESEM device. The resistance measurements were performed with a Hewlett-Packard multimeter connected to a 100 cm^3 size gas chamber with probe connections. MKS flow controllers were used to control the gas pulses injected to the gas measurement chamber. The carrier gas used was 20 % O_2 in N_2 and measurement temperatures were 200 °C and 350 °C.

3. Structural Characterization

X-ray diffraction studies of the different post-annealed metal oxide layers are shown in Fig. 1. In Fig. 1 a), the X-ray diffraction data of WO_3 layers deposited at $p(O_2)$ = 0.08 mbar and $p(O_2)$ = 0.2 mbar is shown. It is clear from the data that the phase structure of the samples is highly dependent of the deposition parameters. The sample deposited at $p(O_2)$ = 0.08 mbar is composed almost solely of γ-phase WO_3, but in the sample deposited at $p(O_2)$ = 0.2 mbar also a high amount of ε-phase of WO_3 is identified. In the ZnO modified SnO_2 layers and in the V_2O_5 layers, presented in Figs. 1 b) and c), respectively, no differences were found in phase composition, when different O_2 partial pressures were used. All the layers were defined to be composed of the pure metal oxides.

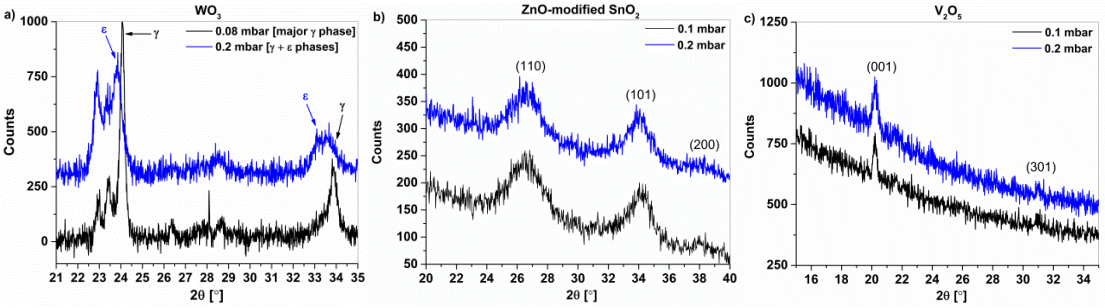

Fig. 1. X-ray diffraction data of a) the WO_3 layers, b) ZnO modified SnO_2 layers, and c) V_2O_5 layers.

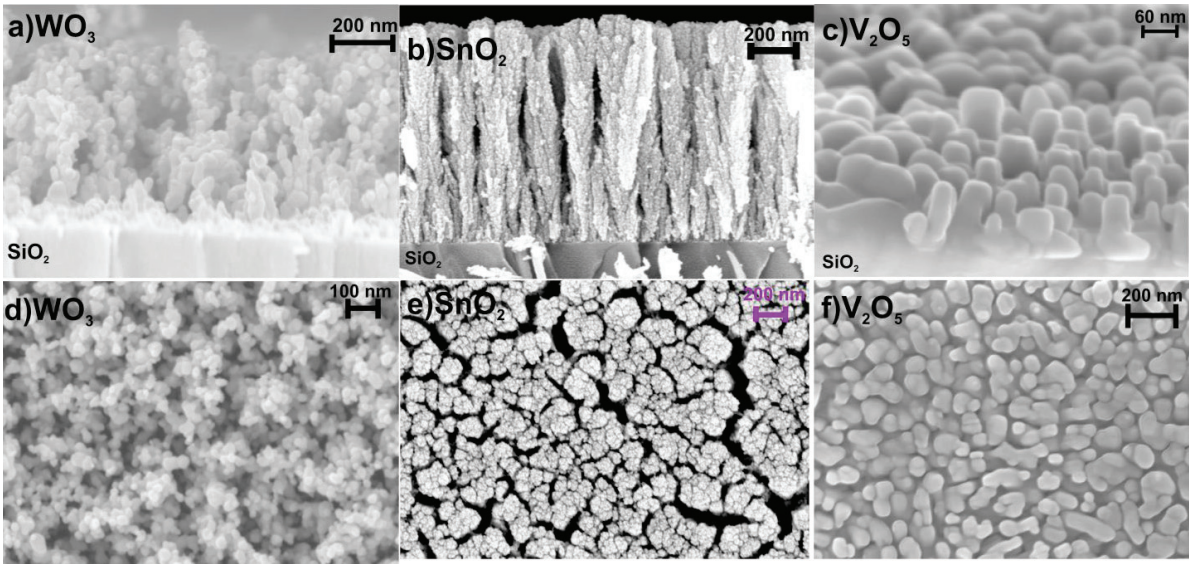

Fig. 2 SEM cross-section micrographs (a-c) and surface micrographs (d-f) of the metal oxide layers.

Scanning electron microscopy micrographs of the metal oxide layers deposited at $p(O_2) = 0.2$ mbar are shown in Fig. 2. The cross-section and the surface micrographs of WO_3 structure are presented in Figs. 2 a) and d), respectively. The layer is composed of small nanoparticles with tubular-like agglomerates on top of the substrate. The high porosity of the layers is also evident. In Figs. 2 b) and e), the cross-section and the surface micrographs of ZnO modified SnO_2 layers are shown, respectively. A very strong fractal-type of growth with nanotree formations can be identified from the graph. The nanotrees are formed of very small nanoparticles ($\varnothing < 20$ nm) and are only a few hundred nanometers wide, and the length of the trees is around 1 micrometer. The cross-section and the surface micrographs of V_2O_5 layers are presented in Figs. 2 c) and f), respectively. V_2O_5 film shows single nanoparticle formations of some pillar-like growth mode. All the layers show high specific surface area, which is advantageous for gas sensing. The SEM micrographs of layers deposited at lower O_2 partial pressure values, *i.e.* $p(O_2) = 0.08$ mbar or 0.1 mbar, are not shown here. However, SEM studies have shown that for all metal oxides presented here, using a lower O_2 partial pressure in the PLD process results to much more dense film structures.

4. Gas Response Characterization

Commercial MEMS microheaters from SGX Sensortech SA were used as the sensor platform for the PLD deposited sensing layers in the gas response measurements. In Fig. 3, examples of the resistance response for the three types of gas sensing layers are shown. It is clearly seen that all three different metal oxide layers exhibited a high sensitivity to selected target gases, *i.e.* NO for WO_3 and ZnO-modified SnO_2, as shown in Figs. 3 a) and b), and NH_3 for V_2O_5, shown in Fig. 3 c). Some instability, in form of drifting resistance baseline, was seen in all samples. The long-term stability of the sensing layers could be improved as well. However, preliminary studies of similar sensing layers, but with higher post-annealing temperature and time, give implications that the long-term stability is improved with the new post-annealing procedure, and still the layer morphology is very little affected by the higher temperature or time in the furnace.

The responses of the sensing layers, defined here as the change of resistance divided by resistance baseline, for different gases at selected temperatures, are shown in Fig. 4. It is clear, that the WO_3 layer, shown in Fig. 4 a), is somewhat selective to NO, at least at higher gas concentrations. The ZnO-modified SnO_2 layer, in Fig. 4 b), has very high sensitivity to both NO, at higher gas concentrations, and to CO. The V_2O_5 layer overall shows a reasonably high sensitivity and selectivity to NH_3.

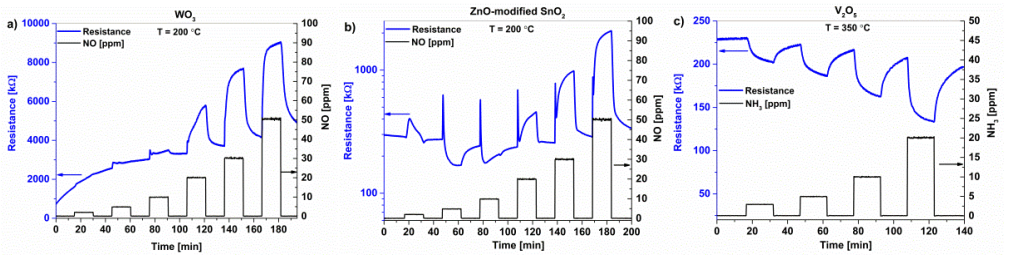

Fig. 3. The change of resistance towards selected gases a) WO_3, b) ZnO modified SnO_2, and c) V_2O_5 layers.

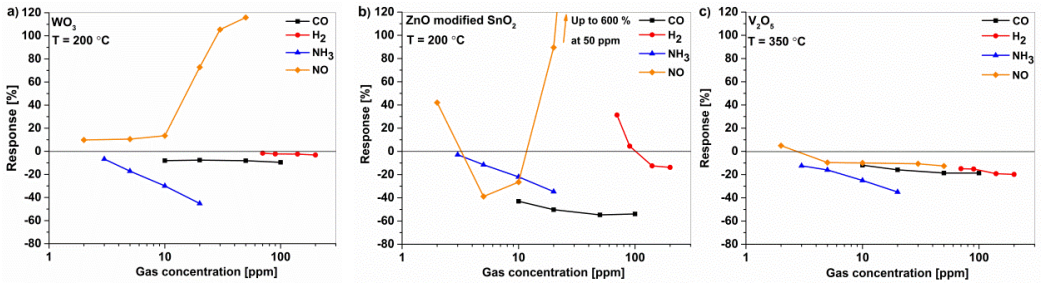

Fig. 4. Examples of gas responses of a) WO_3, b) ZnO modified SnO_2, and c) V_2O_5 layers to various concentrations of CO, H_2, NH_3, and NO. The WO_3 and SnO_2 layers show very good response up to 600 % to 50ppm NO, and the V_2O_5 layers show a response of up to -35 % to 20ppm NH_3.

5. Conclusion

The structure and gas sensing properties of pulsed laser deposited WO_3, ZnO modified SnO_2, and V_2O_5 nanostructures were studied. The WO_3 layers phase composition was dependent on the PLD O_2 partial pressure used, while the O_2 pressure did not affect the phase composition of ZnO-SnO_2 and V_2O_5 layers. From the SEM studies it was concluded, that the morphology of WO_3 layers was composed of nanoparticle agglomerates, the ZnO-SnO_2 layers had fractal-type nanotree morphology, and V_2O_5 layers were composed of individual nanoparticles with pillar-like growth. The gas sensing results showed that the WO_3 layers were sensitive to NO and to some extent also to NH_3 with response in the opposite direction, but inert to CO and H_2. ZnO-SnO_2 layers were sensitive to all tested gases but the response was higher to CO and very high to NO, while the V_2O_5 layers were sensitive and rather selective to NH_3.

Acknowledgements

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