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Room Temperature UV-Enhanced NO_2-Gas Sensing of Doped and Undoped Sol-Gel-Synthesized ZnO

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Abstract:
ZnO is of interest for many applications, e.g. also for gas sensing. Here, sol-gel synthesized, nano-sized ZnO is investigated with regard to its room temperature NO_2 sensing behavior. It is shown that both doping and UV exposure shorten the response and the recovery times of the sensors. NO_2 measurements were carried out with undoped, Sn-doped, and Al-doped ZnO sensors, respectively. The Al-doped samples provide the highest NO_2-response. Furthermore, the effect of dry or humid atmosphere on the sensor response was investigated. The strong humidity influence on the sensor signal almost disappears with UV exposure. Hence, UV-light, nano-sized structure, and proper doping may be the key for room temperature NO_2 sensing.

Key words NO_2, ZnO, UV-enhanced gas sensing, room temperature gas sensing

Introduction

Since gases like NO_2 are harmful for humans, it is important to monitor their concentration by gas sensors to ensure that the immission limits are maintained [1]. A well-investigated material for these sensors is ZnO, which is a n-type semiconductor [1]. Most of the reported ZnO-based sensors need high temperatures [2,3] or cannot detect NO_2 at low ppm-levels [4]. For air quality control measurements, a material is characterized that operates at room temperature and that can detect low NO_2 levels.

Experimental

Zinc-acetate was dissolved in deionized water. For doping, Aluminum-nitrate or Tin-chloride was added. After heating to 78 °C, ethanolamine was added and a pH-value of 7 was adjusted and stirred for 2 h. The white solid product was filtered and dried for 3 h in air. Afterwards, the powder was calcined at 550 °C and processed to a paste. The paste was applied on top of an interdigital electrode structure on alumina and fired at 450 °C. The morphology of the powders was characterized by SEM. The sensor response was measured in a gas sensor test chamber. The sensor resistance was measured by an impedance analyzer. The gas composition varied from dry to humid (2 vol.% H_2O) synthetic air. 0.7, 1.5, or 2.2 ppm NO_2 were added stepwise. The NO_2-concentration was determined by a chemi-luminescence detector (CLD). Three UV-LEDs (365 nm) with 0.8 mW/cm^2 irradiation intensity acted as an UV source.

Results and Discussion

In Fig. 1, the morphology of undoped and doped ZnO is shown. Undoped (Fig. 1a) and Sn-doped powders (Fig. 1b) show similar morphology with almost spherical crystals of about 200 nm in diameter. Al-doping leads to

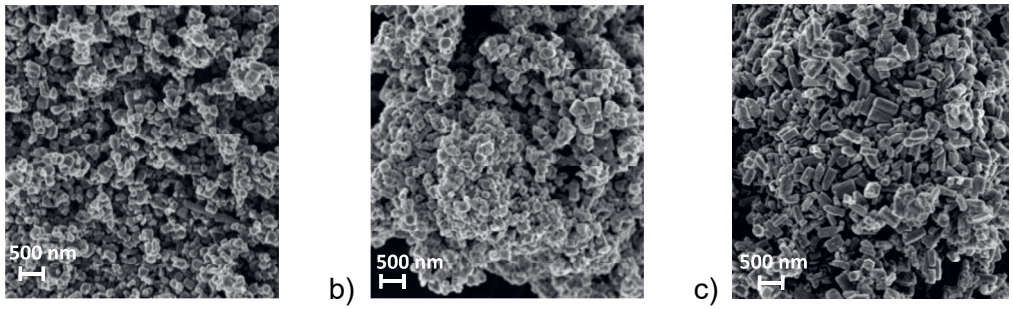

Fig. 1. SEM-images of the powders a) undoped ZnO b) 1 % Sn-doped ZnO c) 1 % Al-doped ZnO

prism shaped crystals with 500 nm in length and 150 nm in diameter (Fig. 1c). Al seems to enhance the crystal growth along the c-axis. So, there is a higher amount of [10$\bar{1}$ 0]-(non-polar) planes than in spherical shaped crystals.

The room temperature NO_2 sensor responses of different dopants under UV light in dry synthetic air are shown in Fig. 2a. The signals for undoped and Sn-doped ZnO are almost the same. Al doping leads to a higher response (Fig. 2 a). It is possible that the NO_2 adsorption only occurs on the non-polar [10$\bar{1}$ 0]-planes [5] that are formed preferably in Al-doped ZnO. When the atmosphere changes from dry air to humid air (Fig. 2b), the sensor responses of Al-doped ZnO for NO_2 do not differ much.

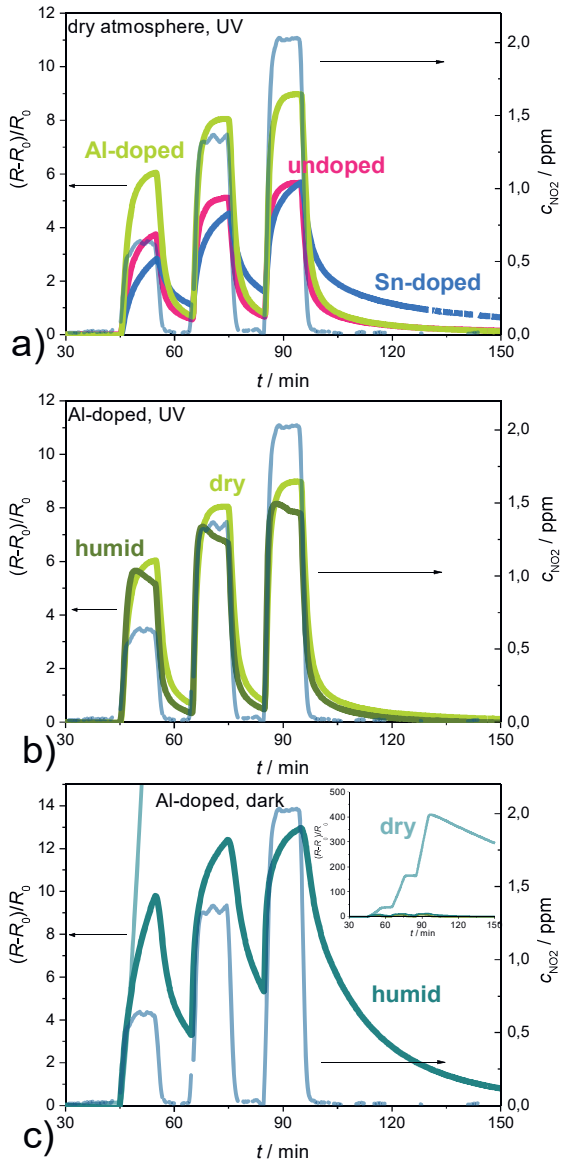

Fig. 2. NO_2-sensor response of a) undoped, Al-doped and Sn-doped ZnO in dry air under UV-exposure b) Al-doped ZnO in dry and humid air under UV-exposure c) Al-doped ZnO in dry and humid air without UV-light

Without UV exposure (Fig. 2c) for Al-doped sensors, the sensor behavior shows a big difference for dry and humid air. Although the response and recovery times in humid air are high, the sensor shows the signal of a concentration gas sensor. Contrary to this, in dry air the sensor behaves like a dosimeter (amount gas sensor) [6]. Compared to UV-exposed signals, the sensor response is without UV higher but recovery and response is slower. Since UV radiation generates electrons and holes in the ZnO, the holes can recombine with the electrons that are involved in the adsorption of O_2 or NO_2. This may cause a higher desorption rate and may lead to a lower recovery time. In addition, the sensor response is smaller under UV-light, probably because fewer adsorbed gas molecules exist simultaneously at the ZnO surface.

Conclusion

It is shown that Al-doping of ZnO enhances the room temperature NO_2-sensing properties. Further UV-light reduces response and recovery times of the sensor, with a huge response even for 1 ppm NO_2. Because of high sensor response for small ppm-levels it can be expected that the material works even for ppb levels. This has to be investigated in further studies.

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