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Influence of Oxygen Impurities on the CO/H_2 Selectivity of GaN Based Gas Sensors

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Abstract:
We report on the influence of oxygen impurities on the gas sensing properties of gallium nitride based chemiresistors, once prepared by using synthesized GaN from nitridation of Ga_2O_3 and once by using a commercial GaN. Time dependencies of the resistance for untreated- and ammonia treated-GaN sensors exposed to carbon monoxide (CO) and hydrogen (H_2) in pure nitrogen at 530 °C is investigated. The untreated GaN sensors show high response towards both CO and H_2 whereas for ammonia treated GaN sensors the sensitivity towards CO is dramatically reduced. The decrease in CO sensor response for ammonia treated GaN sensors is attributed to a decrease in the wt.% of contaminated oxygen in as synthesized- and commercial-GaN after their treatment in dry ammonia.

Key words: Gallium nitride, oxygen impurities, selective hydrogen sensors, ammonia treatment.

1 Introduction

Successful development of gas sensors for commercial purpose should possess three important characteristics: sensitivity, selectivity and stability [1]. Metal oxide gas sensors based on SnO_2, ZnO, TiO_2, WO_3 and In_2O_3 show high sensitivity but poor selectivity when used in pure form. In general there are four ways of obtaining selectivity in semiconductor gas sensors with various degree of success [2]: (i) the use of catalysts and promoters, (ii) the application of a temperature control/modulation, (iii) the addition of specific surface additives, and (iv) the use of a physical or a chemical filters over the sensing material.

In the present work, we report on a novel approach demonstarting highly selective H_2 gas sensors obtained by treating GaN as a gas sensing material under dry ammonia.

2 Experimental

2.1 *GaN synthesis and sensor preparation*: GaN was synthesized by the nitridation of commercial gallium oxide (β-Ga_2O_3) in dry ammonia at 900°C over 24 h [3]. The as obtained GaN powder was screen-printed on alumina substrates provided with interdigitated Pt electrodes – for the readout of the electrical properties – on the front side and Pt heater – for the operation at well controlled temperatures – on the back side. Finally the sensors underwent a thermal treatment under nitrogen atmosphere in a moving belt oven (400-600°C). A post-deposition ammonia treatment of the GaN screen-printed sensors was performed under dry ammonia at 800 ºC for 6 h. Same deposition and NH_3-treatment procedure was applied for gas sensors based on commercial GaN powder (Sigma-Aldrich)

2.2 *Characterization and sensor tests*: X-ray powder diffraction data were collected on a D8 Advance diffractometer (Bruker, USA) with Cu Kα radiation in the reflection scanning mode in the 2θ range of 25–80°. The nitrogen and oxygen content in GaN powders and sensors before and after additional ammonia treatment was measured with N/O analyzer (Leco, Type TC-436) using a hot gas extraction method. Untreated- and ammonia treated-GaN based gas sensors were mounted in a gas chamber which is connected to a computer controlled gas mixing system. Sensing performance was tested in an almost oxygen-free gas

atmosphere (< 3 ppm; below the detection limit of the oxygen gas analyzer ZIROX SGM). The GaN sensors were exposed to CO (10, 20, 120 ppm) and H_2 (40, 400, 900 ppm) for two hours in dry nitrogen (Type 5.5) in a flow of 500 sccm at an operation temperature of 530°C. All measurements were performed several times until reproducible results were obtained.

3 Results

We have found that highly selective hydrogen sensors based on GaN can be obtained by post-deposition treatment of the oxygen-contaminated GaN under dry ammonia. The as synthesized- and commercial-GaN sensors show comparable response to CO and H_2 (Fig. 1). Surprisingly, the post-deposition ammonia treatment of sensors leads to the drastic reduction of sensor response to CO.

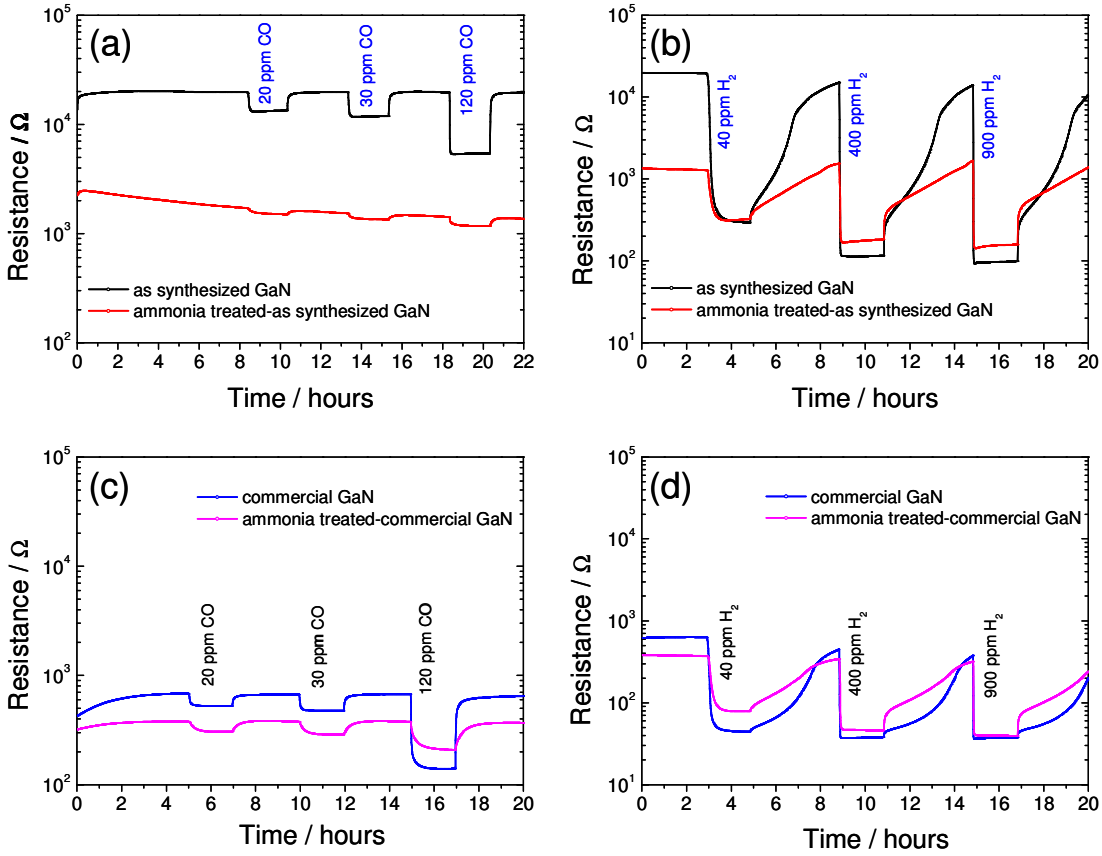

Fig. 1: Transient response of (a,b) as synthesized- and ammonia treated-as synthesized GaN sensors, and (c,d) commercial- and ammonia treated-commercial-GaN sensors during exposure to CO and H_2 in nitrogen at 530 °C.

No significant differences in the X-ray diffraction patterns (Fig. 2 a) are found for the as synthesized- and ammonia treated-as synthesized-GaN powders. Low intense peaks of Ga_2O_3 are found for commercial GaN powder; these peaks disappear after NH_3-treatment (Fig. 2 b). Nevertheless, a difference in the oxygen content is found by the elemental analysis. As synthesized- and commercial-GaN powders show oxygen contamination of about 2.8 and 4.9 wt.%, respectively, which is reduced to about 1.6 and 2.4 wt.%, respectively, after treating in ammonia (Table 1). The loss of CO sensitivity for ammonia treated GaN sensors is attributed to the removal of either amorphous (in as synthesized GaN) or crystalline (in commercial GaN) surface oxide layer during ammonia treatment that results in fresh GaN surface which is not sensitive towards CO.

Tab. 1: Elemental composition of the as synthesized- and commercial-GaN powders before and after treatment under ammonia.

Samples	N / wt. %	O / wt. %
as synthesized GaN	14.9	2.8
ammonia treated-as synthesized GaN	15.9	1.6
commercial GaN	13.8	4.9
ammonia treated-commercial GaN	15.0	2.4

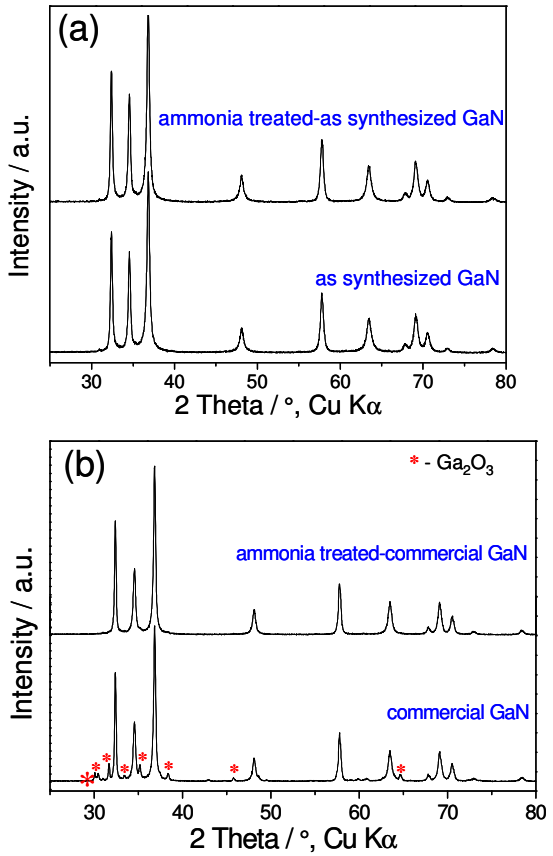

Fig. 2: X-ray powder diffraction patterns of (a) as synthesized- and ammonia treated-as synthesized-GaN powders, (b) commercial- and ammonia treated-commercial-GaN powders.

4 Conclusions

In summary, the effect of ammonia treatment of GaN based sensors has been investigated. Untreated GaN sensors show high response towards both CO and H_2 in the almost absence of oxygen whereas for ammonia-treated GaN based gas sensors the sensitivity towards CO is significantly reduced.

Acknowledgements

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