Response of Gallium Nitride Chemiresistors to Carbon Monoxide is due to Oxygen Contamination

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Supporting Information Placeholder

ABSTRACT: We report on the influence of oxygen impurities on the gas sensing properties of gallium nitride (GaN) chemiresistors. As shown by XRD, elemental analysis and TEM characterization, surface oxidation of GaN – for example, upon contact to ambient air atmosphere - creates an oxidative amorphous layer which provides the sites for the sensing towards CO. Treating this powder under dry ammonia at 800 °C converts the oxide layer in nitride and consequently the sensing performance towards CO is dramatically reduced for ammonia treated GaN gas sensors. Hence the response of GaN sensors to CO is caused by oxygen in the form of amorphous surface oxide or oxynitride.

Keywords: chemiresistors, gallium nitride, carbon monoxide, oxygen, gallium oxide

Nowadays gas sensors based on metal oxides (SnO_2, ZnO, TiO_2, WO_3, In_2O_3, etc.) are widely used for the detection of toxic and combustible gases as well as for air quality control in buildings, vehicles and airplanes.[1-4] Metal nitride (e.g. GaN) sensors are known to be capable of operation in harsh environmental conditions.[5-8] With a wide bandgap of 3.45 eV and strong chemical bonds, GaN combines favorable properties especially for high power, high-frequency, and high-temperature devices. GaN powders and films have been applied for sensing H_2, CO and CH_4.[6-10] Oxygen is a common impurity in GaN that influences significantly electrical and optical properties of GaN-based materials (see ref.[11] and references therein). Besides substitutional oxygen[12], which can occur under typical synthesis conditions, i.e. heat treatment under ammonia or CVD process, an oxide passivation on the surface of freshly produced GaN develops over time. GaN surfaces are becoming firstly covered with amorphous GaO_x layer that finally crystallizes to polycrystalline Ga_2O_3 film.[13] Passivation oxide layer on GaN surfaces is a well known effect studied in much detail in previous works.[11] However, the effect of surface oxygen impurities as well as surface oxide layer on the gas sensing properties of GaN remains still unclear, even if there are some indications of that.[10, 14]

In the present work, we study the influence of oxygen impurities in GaN sensors applied for CO detection in the oxygen-free atmosphere. GaN specimens were prepared from as-synthesized oxygen-contaminated GaN powder and post-treated under dry nitrogen and dry ammonia gases as well. The latter is known to be an effective method for the removal of oxygen from GaN surfaces.[15]

Table 1 displays the results of elemental analysis and phase composition of untreated ("GaN"), nitrogen ("GaN/N_2") and ammonia ("GaN/NH_3") treated GaN powders.

Table 1. Elemental analysis and phase composition of as-received (untreated) GaN powders and heat-treated specimens in N_2 and NH_3 gases.

Specimen	Synthesis/ treatment conditions	N (wt.%)	O (wt.%)	nO/ (nO+nN) %	Phase composition (XRD)	Phase composition (TEM)
"GaN"	β-Ga_2O_3 treated in NH_3 (900 °C, 24 h) and kept in ambient air for about six months	14.9	2.8	14	GaN	GaN + Ga_2O_3 + amorphous surface
"GaN/N_2"[a]	"GaN" treated in N_2 (600 °C, 2 h)	15.0	2.7	13	GaN	not studied
"GaN/NH_3"	"GaN" treated in NH_3 (800 °C, 6 h)	15.9	1.6	8	GaN	GaN + Ga_2O_3[b] + amorphous surface

[a] "GaN" specimen treated under conditions (N_2) applied for the firing of the sensors (for details, see experimental methods in SI); [b] smaller Ga_2O_3 particles if compared to untreated "GaN".

Let us note that the oxygen content of the "GaN/N_2" specimen remains similar to that of "GaN" sample, indicating that, as intended for, the treatment in dry nitrogen, in the conditions applied for the sensors preparation does not modify the chemical composition of the sensors. However, a significant difference in oxygen content is observed in the "GaN" and "GaN/NH_3" specimens. GaN specimen synthesized from β-Ga_2O_3 under ammonia at 900 °C and stored in air for about six months possesses about 2.8 wt.% of oxygen, which is reduced to about 1.6 wt.% after treatment in ammonia at 800 °C for 6 hours.

No difference in the X-ray diffraction patterns is observed for the "GaN", "GaN/N_2", and "GaN/NH_3" powders (Figure 1) as well as for GaN sensors before and

after sensing tests under CO (20-120 ppm in N_2) at 530 °C (Figure 2).

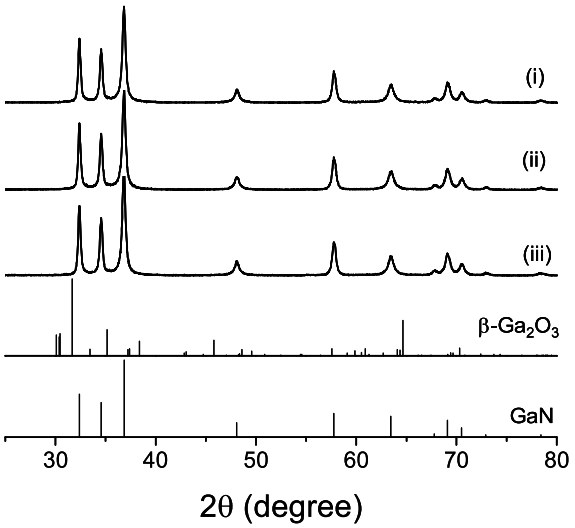

Figure 1. X-ray powder diffraction (XRPD) patterns of "GaN" (i), "GaN/N_2" (ii), and "GaN/NH_3" (iii) specimens (see Table 1). The diffraction patterns of β-Ga_2O_3 (ICDD PDF No. 43-1012, monoclinic, space group C2/m, a = 12.23 Å, b = 3.04 Å, c = 5.80 Å) and GaN (ICDD PDF No. 50-0792, hexagonal, space group $P6_3mc$, a = 3.18907 Å, b = 3.18907 Å, c = 5.1855 Å) are shown at the bottom.

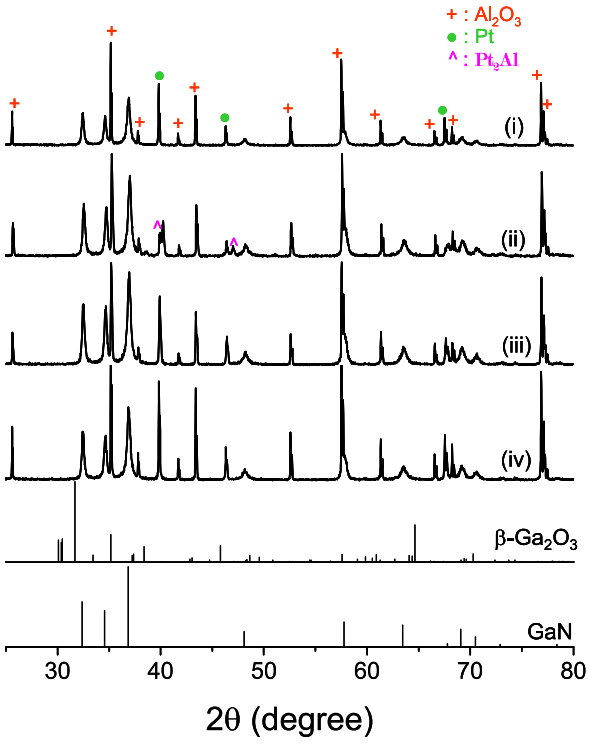

Figure 2. X-ray powder diffraction (XRPD) patterns of GaN layers on sensor substrates before and after gas sensing measurements: (i) and (ii) represent "GaN" coated sensor substrates before and after sensing measurement, respectively; (iii) and (iv) represent "GaN/NH_3" coated sensor substrates before and after sensing measurement. Here, it should be noted that XRD characterization done on the GaN coated sensor substrates before sensing measurement, specimen (i) and (iii), are different sensor samples than those after sensing measurements, specimen (ii) and (iv). Al_2O_3 and Pt reflections are due to sensor substrate and electrodes.

Figure 3 shows the TEM images of "GaN" and "GaN/NH_3" specimens. For both "GaN" and "GaN/NH_3" powders an amorphous surface layer is observed. Surface Ga_2O_3 particles are seen for "GaN" powder (Figure 3A,B), as well as for "GaN/NH_3" powder (Figure 3C,D,E). However, larger particles were observed via TEM in the untreated powders compared to the ammonia treated sample, where the particles are in the order of 2–5 nm.

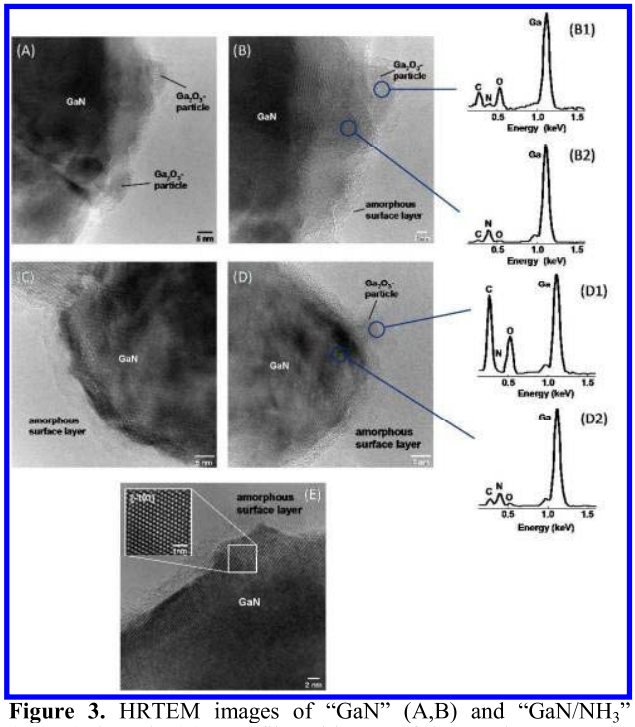

Figure 3. HRTEM images of "GaN" (A,B) and "GaN/NH_3" (C,D,E); inset in (E) FFT filtered image of the matrix near to the surface of "GaN/NH_3" specimen. Corresponding EDS spectra are shown in (B1, B2, D1, D2).

EDS chemical analysis reveals that the particles on the surface in both samples are Ga_2O_3 which are not present in the XRD diffraction pattern (Figure 1), whereas the matrix in the close vicinity of the particles is GaN (see FFT filtered inset in Figure 3E). The amorphous surface layer shows peaks in EDS which can be assigned to gallium and oxygen. Because the surface layer also contributes to the analysis done at the bulk sample, the EDS will also show a minor amount of oxygen. The carbon peaks are due to contamination during the measurement and are more pronounced for the small particles. Our finding is similar to the mechanism of GaN surface oxidation as proposed in other works [13, 16, 17], which show the formation of a Ga_2O_3 layer covering GaN particles.

To assess the performance of "GaN" and "GaN/NH_3" sensors in oxygen free-conditions, gas sensing properties of the sensors were studied at 350°C and 530 °C towards different CO (10–120 ppm) concentrations (Figure 4A,B). A number of significant differences are observed between "GaN" and "GaN/NH_3" sensors. Upon CO exposure, reasonable resistance changes are measured for the "GaN" sensor with rather fast response and recovery times at both

temperatures, whereas for the "GaN/NH_3" coated sensor only a weak response is observed at 530°C. This effect was reproducible and was observed repeatedly on several sensors. Sensor signal towards CO is dramatically increased when oxygen in GaN is present (Figure 4C). Sensor signal for "GaN/NH_3" sensors were 3-10.4 times (at 350 °C) and 1.3-3.1 times (at 530 °C) weaker than "GaN" sensors in the CO (20-120 ppm).

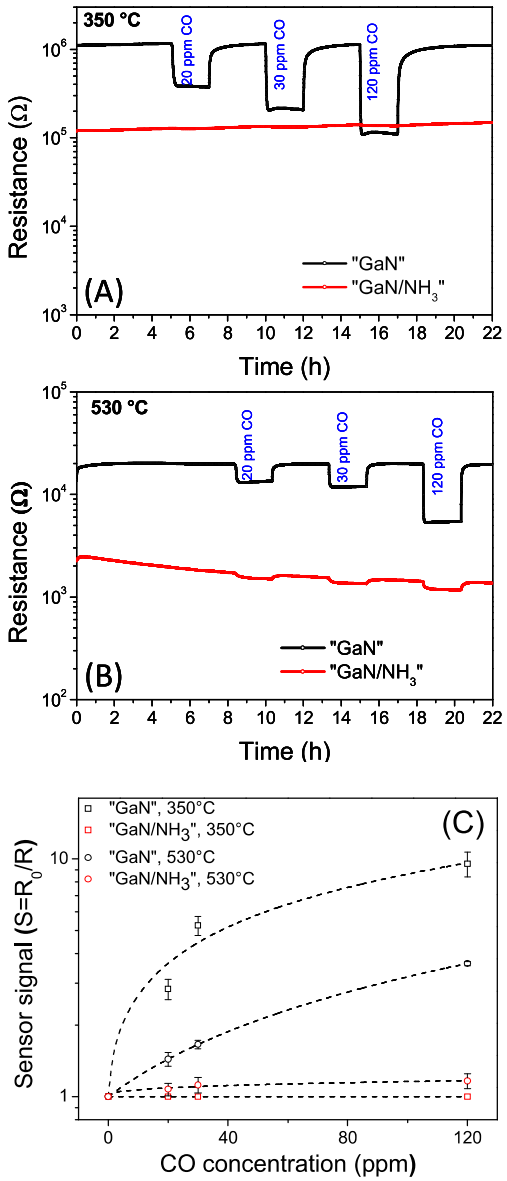

Figure 4. Transient response (A,B) and sensor signals ($S=R_0/R$) (C) of "GaN" and "GaN/NH_3" sensors during exposure to CO (20, 30 and 120 ppm) in nitrogen at 350 °C and 530 °C; R_0 is baseline resistance whereas R is the resistance under different CO concentrations. In (c) the experimental points averaged over three measurements are fitted with a function $S=1+aC^b$ where a=0.36, 0.03, 0.02 and b=0.66, 0.36, 1.00 for "GaN" sensors at 350 and 530 °C, and "GaN/NH_3" sensors at 350 °C, respectively.

As shown recently[18], the stoichiometric GaN undergoes surface amorphisation, the amorphous phase (a-GaN(O) afterwards) is stabilized herewith by the oxygen incorporation. Oxygen resides in dislocations and grain boundaries rather than substitutes for nitrogen in the bulk. Interestingly, we observe an amorphous surface in both, i.e. "GaN" and "GaN/NH_3" that show quite remarkable difference in the gas sensing properties. The main difference we found is the oxygen content, i.e. ca. 14% in "GaN" and ca. 8% in "GaN/NH_3" specimens and a decrease in the amount and size of Ga_2O_3 particles. Therefore, we conclude that the difference in the gas sensing properties of "GaN" and "GaN/NH_3" is caused by the local structural arrangements that involve Ga–N and Ga–O bonds. GaN consists of slightly distorted [GaN_4] tetrahedral units with the hybridized sp^3 orbitals that form in-plane and out-of-plane bonds (Figure 5A). The X-ray Absorbance Spectroscopy (XAS) results indicate that the [GaN_4] tetrahedra are modified in the amorphous films due to the preferential substitution of the out-of-plane components, as a result oxygen-substituted polyhedra appear at the GaN surface.[19, 20] As shown by Ga L_3-, N K- and O K-edge XAS, the coordination symmetry of gallium in a-GaN(O) depends on the amount of oxygen incorporated, i.e. with increasing oxygen amount the tetrahedral [$Ga(N,O)_4$] units are transformed into distorted octahedral [$Ga(N,O)_6$] units that are characteristic for gallium oxynitride. A full substitution of N by O subsequently forms β-Ga_2O_3 (Figure 5A). Effectively, both [$Ga(N,O)_4$] and [$Ga(N,O)_6$] units look amorphous in XRD characterization (Figure 1). Figure 5B displays a model of transformation stages of GaN specimens studied in the present work. The decrease in the oxygen content in GaN powder from ca. 14 to 8% after its treatment under ammonia at 800 °C is indicated by the decrease in the amount and size of Ga_2O_3 particles and by the decrease of thickness of the surface amorphous gallium oxynitride layer.

Based on results of XRD, elemental analysis and TEM characterization of GaN powders we can propose that when as-synthesized GaN powder is stored under ambient air condition, surface oxidation of GaN creates an oxidative amorphous layer (that does not appear in the XRD pattern) which provides the sites for the sensing towards CO. Treating this powder under dry ammonia at 800 °C destroys the oxidative layer (converting to nitride layer) and consequently the sensing performance towards CO is dramatically reduced for ammonia treated GaN gas sensors.

Therefore, it is logically coherent to suggest that distorted octahedral [$Ga(N,O)_6$] and [GaO_6] units in untreated a-GaN(O) with higher oxygen content and β-Ga_2O_3, respectively, provide sensitivity to CO, and tetrahedral [$Ga(N,O)_4$] with lower oxygen content in ammonia treated GaN do not. Our assumption is confirmed by the similar response to CO of β-Ga_2O_3 and untreated-GaN [please refer to supporting information (SI)] that indicates a similar detection mechanism for both, i.e. a chemisorption path that leads to an accumulation layer due to CO^+-adsorbates on [$Ga(N,O)_6$] /[GaO_6] surface that donate electrons to the conduction band of GaN increasing in this a conductivity of the material. [21] The effect we observe resembles a significant increase in CO sensitivity on surface-nitridated Ga_2O_3 nanowires[22] thus indicating an

activity of mixed-bond [Ga(N,O)$_6$] units in CO detection both on partially oxidized GaN or partially nitridated Ga_2O_3 materials.

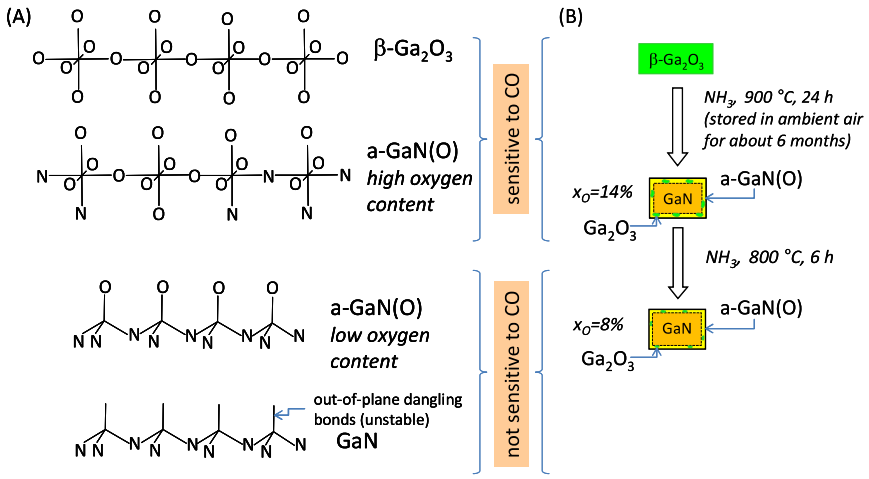

Figure 5. (A) Schematic representation of the local structure model representing the relationship between interaction of oxygen with GaN sensors and their sensitivity to CO. The tetrahedral coordination of Ga remains intact when a low amount of oxygen is incorporated. Interaction of oxygen with out-of-plane dangling bonds lead to the formation of amorphous gallium oxynitride with tetrahedral a-GaN(O):GaN_3O units that eliminate out-of-plane Ga-N bonds but do not influence the GaN bulk structure. Further increase of the oxygen amount leads to the formation of a distorted amorphous gallium oxynitride with octahedral a-GaN(O):GaN_2O_2 units. Complete substitution of N by O yields in distorted octahedral GaO_6 units. (B) Schematic representation of different stages of transformation process, from ammonolysis of Ga_2O_3 to GaN followed by surface oxidation of as-synthesized GaN under air after storing for 6 months and finally re-treatment of "GaN" under ammonia at 800 °C for 6 h; a-GaN(O) represents amorphous gallium oxynitride layer formed due to surface oxidation.

In summary, the effect of ammonia treatment of as-synthesized GaN based sensors on their gas sensing properties has been investigated. Untreated GaN sensors show high response towards CO in oxygen-free conditions whereas for ammonia treated GaN based gas sensors the sensitivity towards CO is lost at 350 °C and significantly reduced at 530 °C. This study gives the direct evidence of the oxygen implication in the CO detection process in oxygen-free conditions of GaN gas senors. It also points out that for non-oxides based gas sensors, prone to oxidation when exposed to air, accurate characterization of the surface chemistry is of crucial importance..

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI…: GaN synthesis, sensor fabrication, characterization methods, gas sensing performance of Ga_2O_3 based sensors.

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SYNOPSIS TOC