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Chemically Sensitive Photoluminescence of InGaN/GaN Nanowire Heterostructure Arrays †

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1. Background

III-nitride semiconductors (AlGaN, GaN and InGaN) have received considerable attention in various fields ranging from high-frequency and high-temperature electronics [1] to LED lighting technologies [2]. Interesting applications also arise in the fields of gas, chemical and biosensors [3,4] and in photo-electrochemical power conversion [5].

2. Experiment

We have studied the photoluminescence (PL) response of InGaN/GaN heterostructure nanowire arrays (NWA) while being exposed to different kinds of oxidizing and reducing gases as well as to humidity (Figure 1a) [6–10]. As III-nitrides tend to form thin, native surface oxide layers when exposed to ambient air, their chemical interactions are similar to those on more traditionally studied kinds of metal oxides (MOX). As InGaN/GaN NWAs exhibit efficient photoluminescence up to temperatures of 200 °C and more, PL measurements can be performed at temperatures approaching those of conventional resistive MOX gas sensors. As localized adsorbate-adsorbent reactions are directly answered by a local PL output, the PL response of InGaN/GaN NWAs provides a more direct view onto surface adsorption processes than conventional resistive MOX gas sensors.

3. Results

Figure 1b shows that our NWAs exhibit a quenching response when exposed to O_2 in a N_2 background. Quenching responses are also observed when tiny concentrations (ppm and below) of NO_2 and O_3 are admixed to synthetic air (SA) [6,10]. Enhancing responses to water vapor can be observed when H_2O exposures are performed in N_2 (Figure 1c) and when these are maintained for prolonged periods of time and at high illumination levels [7,10]. We attribute this enhancing behavior to the photo-electrochemical generation of passivating H^+ and OH^- fragments. Reducing gas species (e.g. EtOH) give rise to enhancing responses only when the NWAs are operated in SA and at elevated temperatures. No responses to reducing gases are observed when these are applied in inert N_2 backgrounds. Reducing gas species therefore are detected in an indirect manner by consuming quenching oxygen adsorbates and by forming enhancing H_2O ones as these interact with oxygen species co-adsorbed in reactive backgrounds of ambient or synthetic air [8,10].

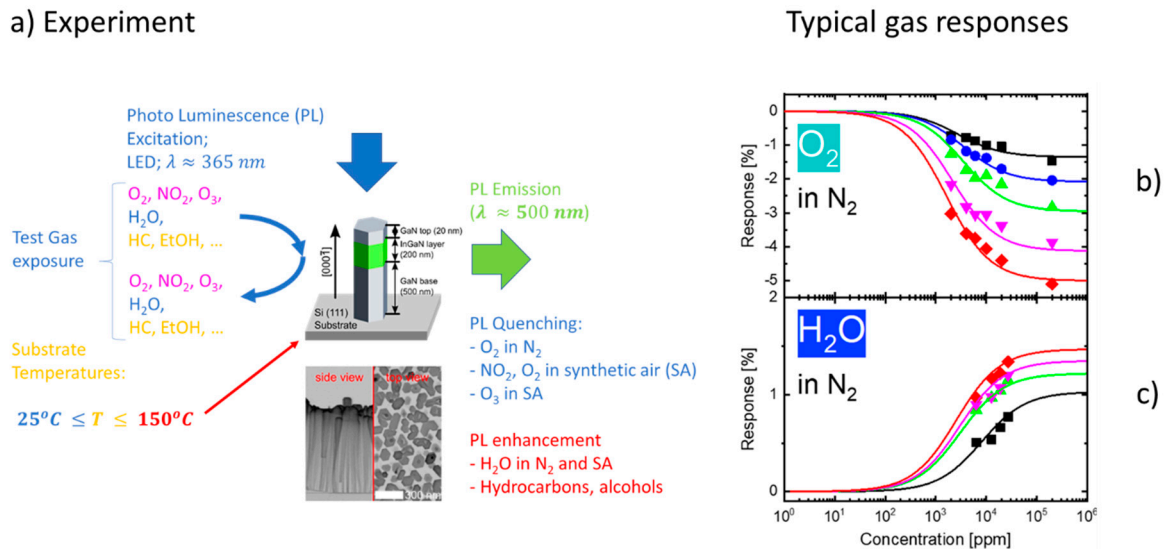

Figure 1. (**a**) Detection of adsorbate-induced changes in the PL emission response of InGaN/GaN nanowire heterostructure arrays (NWA); (**b**,**c**) typical PL response data as a function of the applied gas (vapor) concentration. Full lines represent fits to Langmuir adsorption isotherms (Equation (1)). Differently colored symbols/lines correspond to increasing NWA temperatures (black: 25 °C; red: 150 °C).

A characteristic observed across all kinds of analytes is that the concentration dependence of the PL response, $R_{PL}(p_{gas}, T)$, consistently follows Langmuir isotherms which are easy to interpret regarding adsorbate-specific adsorption energies E_{ads}:

$$R_{PL}(p_{gas}, T) = R_{PL\_sat} \frac{p_{gas}}{p_{gas} + P_{00}\, exp\left[-\frac{E_{ads}}{k_B T}\right]} \; ; \quad P_{00} \approx 10^{12}\ Pa. \tag{1}$$

A second important parameter is the position of the gas sensitivity window, i.e. the range of gas partial pressures in which gas-induced changes in the PL response can be observed. A convenient parameter that characterizes this position is the value of $p_{gas} = p_{1/2}$ at which the PL response takes on half of its saturation value R_{PL_sat}.

Regarding both parameters, the most important observations are the following:

(i) For a given NWA operation temperature T, the value of $p_{1/2}$ is exponentially dependent on E_{ads}, i.e. small changes in E_{ads} give rise to huge changes in gas sensitivity [6,10];

(ii) For a given sensor operation temperature T, the value of E_{ads} for a given adsorbate scales with the electron affinity, E_A, of the adsorbate [6,10]. The value of the electron affinity is defined as the energy gained upon attaching an electron (e^-) to an adsorbate species X: $X + e^- \rightarrow X^-$;

(iii) For each analyte studied the best-fitting value of E_{ads} is not an adsorbate-specific constant but rather a linear function of the sensor operation temperature. This peculiar behavior can be explained by assuming that test gases compete with background gases for common adsorption sites [9,10].

A full account of our data will be represented in reference [10].

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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