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Adsorption phenomena lie at the heart of understanding semiconductor gas sensors. The most widely studied kind of gas sensors are metal oxide sensors which respond via resistance changes to changes in the ambient gas concentration. A key problem in the analysis of gas sensor behavior is that the effects of adsorption are not readily reflected in the experimentally observable resistive gas response as the electronic transport through such porous and nanocrystalline sensing layers can depend in manifold ways on the stoichiometry and the morphologies of the sensing layers. In an attempt at providing a much more direct view onto the effects of gas adsorption on semiconductor surfaces we have studied the photo-luminescence (PL) response of InGaN/GaN nanowire arrays (NWA) with naturally oxidised surfaces. Such NWAs exhibit an efficient photoluminescence which persists to temperatures of 200℃ and beyond, which additionally exhibits chemical sensitivity as the NWAs are exposed to gases or liquids [1-5]. Gas sensing tests on such arrays reveal both quenching and enhancing PL responses, which indicates that the native PL response of such NWAs is controlled by native defects at the nanowire surfaces which become modified as reactive gases adsorb on these defects. A very interesting observation is that the concentration dependence of the PL response of all kinds of analytes investigated so far (O2, NO2, O3, H2O, EtOH) is that it consistently follows Langmuir-type isotherms which are easy to interpret regarding adsorbate-specific adsorption energies. A surprising finding is that best-fitting adsorption energies do not reveal as species-dependent constants but rather as linear functions of temperature with species-dependent slopes. We show that this behaviour can be explained by a competition of test gases and background gases for common adsorption sites on the NWA surfaces. A particularly interesting gas species is water vapour, which naturally forms quenching adsorbates which transform into enhancing ones as water vapor exposures are prolonged under conditions of moderate surface temperature and under intense UV light illumination. Reducing gases such as H2, aliphatic hydrocarbons and alcohols do not exhibit any intrinsic ability of modifying the PL yield. Such species, rather, seem to be detected in an indirect manner by consuming quenching oxygen adsorbates and by forming enhancing H2O ones as these interact with oxygen species co-adsorbed in reactive backgrounds of ambient or synthetic air. Regarding ongoing research, a very promising aspect is that PL probing of surface adsorption phenomena forms a natural complement to existing technologies of in-operando spectroscopies which are increasingly employed in gas sensor research. Such research is likely to reveal microscopic information on surface adsorption processes which is important for optimizing the operation of gas sensors, catalysts and photoelectrochemical solar cells.

Keywords: III-nitride semiconductors, nanowires, photoluminescence, gas adsorption

Summary

Results are relevant for understanding, designing and optimizing UV-activated low-temperature metal oxide gas sensors.

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