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Opto-chemical sensor system for the detection of H_2 and hydrocarbons based on InGaN/GaN nanowires

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ABSTRACT

We report on an all-optical sensor system that employs InGaN/GaN nanowires (NWs) as opto-chemical transducers. The NWs, grown by plasma-assisted molecular beam epitaxy on low-resistivity n-type Si (1 1 1) substrates, exhibit an efficient room-temperature photoluminescence (PL) that persists up to about 200 °C. After deposition of a thin (5 nm) catalytic Pt-film onto the NWs the PL intensity rises when the NWs are exposed to small concentrations of hydrogen and hydrocarbons. The gas response of the NWs was analyzed using an integrated sensor system with fiber-coupled excitation from a GaN-based power LED emitting at 365 nm and a fiber coupled photo multiplier tube for detection. With this setup, H_2 concentrations as low as 200 ppb and C_2H_2 concentrations as low as 5 ppm could be detected when the transducers were operated at temperatures around 80 °C. This opto-chemical transducer principle is best suited for safety-critical applications where a reliable media separation is required.

1. Introduction

Hydrogen (H_2) and hydrocarbons (HC) are important carriers of energy. These energy carriers, however, become safety hazards when they are released in an uncontrolled manner into the environment. Once mixed with atmospheric oxygen (O_2) these gases can form combustible and explosive atmospheres. Lower explosive limits (LEL) of H_2/air and HC/air mixtures emerge when H_2 and HC concentrations in the order of 3–5% are reached. In order to avoid such situations, leak monitoring is required whenever H_2 and HC carrying installations are operated inside confined spaces. Possible applications in the aeronautic domain are the detection of leaks in fuel and hydraulic lines or the safety monitoring of fuel cell auxiliary power units in commercial aircrafts. In order to be useful as leak monitoring devices, H_2 and/or HC sensors require high sensitivity, good selectivity and reasonably short response times. In addition, leak monitoring sensors should not form ignition sources by themselves when leaks have actually occurred and when potentially combustible atmospheres have already built up.

Over the past decades a wide variety of H_2 and HC gas sensors has evolved. These include heat conductivity sensors, pellistors, and metal-oxide-semiconductor (MOS) field effect gas sensors [1]. This latter kind of sensors was first introduced by Lundström et al. [2] and such sensors have undergone many refinements since that time. Whereas the first MOS gas sensors were fabricated on silicon substrates, newer versions employed wide-bandgap semiconductors such as silicon carbide (SiC) [3] or III-nitride materials [4]. Due to the much larger bandgaps, SiC and III-nitride devices allow higher sensor operation temperatures to be attained. In this way gas sensitivities not only to H_2 but also toward a wider variety of gases could be demonstrated [5]. The higher sensor operation temperatures also enabled much shorter sensor response times. In the case of SiC devices, for instance, response times as short as milliseconds could be attained at around 600 °C [6]. A common feature of all types of MOS gas sensors studied so far is that these are electronically interrogated junction devices, which require electrical powering at the spot of measurement. Furthermore, the detection of H_2 (HC) is performed at temperatures above 200 °C (400 °C), which requires resistive heating of the device. Direct electrical powering of gas sensors for heating and detection, however, is a potential problem as sparking and ignition in combustible atmospheres might inadvertently occur.

In the present paper we report on opto-chemical transducers based on InGaN/GaN nanowires (NWs) that allow sensing of low

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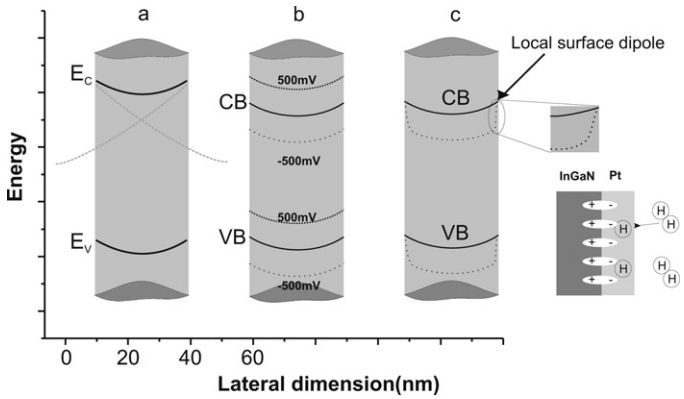

Fig. 1. Position of valence and conduction band edges across a GaN/InGaN NW: (a) NW depleted from free charge carriers by overlapping space charge zones. The result is a negligible surface band bending (SBB) across the NW [14] The solid lines show the conduction and valance band edges inside a fully depleted NW with a diameter of 30 nm. The dashed lines show how the band bending arises from the overlapping of surface depletion layers originating from opposite sides; (b) effect of different surface potentials on the SBB inside a NW; and (c) diffusion of atomic hydrogen through the Pt-layer and improved carrier confinement due to the formation of dipoles at the Pt/InGaN interface. The better confinement leads to a reduced non-radiative recombination at the NW surface.

concentrations of H_2 and HC gases without requiring electrical power on any component in direct contact with a potentially explosive medium. As receptors, these NWs employ the same kind of gas–surface interactions as conventional MOS gas sensors [2–9]; as transducers they use adsorbate-induced changes in the photoluminescence (PL) emission intensity to indicate changes within the gas ambient. Media separation and explosion protection is provided by the fact that PL excitation and PL emission readout can both be carried out through mechanically strong and optically transparent sapphire windows by employing light fiber technology.

2. Opto-chemical transducer principle

Self-assembled GaN-NWs, grown by molecular beam epitaxy [10,11] have been shown to be depleted of free charge carriers, provided that their thickness does not exceed several tens of nanometers [12]. Depletion arises due to carrier trapping at localized surface states within the energy gap. Due to the moderate doping, the spatial extent of surface band bending (SBB) significantly exceeds the NW diameter (Fig. 1a), which results in fully depleted NWs and essentially flat band edges as shown in Fig. 1b. Secondly, the photoluminescence (PL) properties are sensitive to the presence of gases in the ambient atmosphere. Uncoated GaN/AlGaN NWs were shown to be sensitive to oxygen (O_2), and Pt-coated ones to hydrogen (H_2) [12]. The gas sensitivity of the GaN/AlGaN NWs at room temperature and above was interpreted to be due to an increased (O_2) or a decreased (H_2) non-radiative recombination of photoexcited carriers at surface states. The reduced recombination at the surface of Pt coated NWs was attributed to the improved electron confinement caused by the potential drop arising from the O—H dipole layers that form at the Pt/InGaN interface when H_2 molecules dissociate at the Pt surface and as H atoms diffuse to the interface [13] (Fig. 1c).

3. Experimental

3.1. Transducer growth and preparation

In order to make efficient use of the above opto-chemical phenomena in a practically useful sensor device, NWs need to be grown which exhibit a minimum overlap between the PL excitation and the PL emission spectra. In this way the cross talk between the PL excitation and PL emission channels can be minimized. Furthermore, PL excitation must be possible with commercial light emitters. Therefore, InGaN NWs grown on GaN NW templates were employed to realize the opto-chemical transducers sketched in Fig. 2.

The InGaN/GaN NW were grown by plasma-assisted molecular beam epitaxy on (1 1 1) Si substrates and consisted of a GaN base and an InGaN top part (Fig. 2a). The GaN base was grown under N-rich conditions at a substrate temperature of 790 °C. The self-assembly process described in Ref. [15] leads to nanowires with average diameters between 25 nm and 50 nm. For the growth of the InGaN part, the substrate temperature was lowered to 560 °C and N-rich growth conditions were maintained. The lower growth temperature helped to avoid the problem of InGaN decomposition but also lead to a widening of the NW diameters up to about 90 nm at the outer surface of the NW array (Fig. 2b).

The In concentration in the InGaN part was adjusted to approximately 34%, which resulted in a PL peak emission energy of 2.25 eV (Fig. 3) and the band parameters reported in Ref. [16]. Both the GaN- and InGaN-parts of the NW exhibited an efficient PL emission when excited with UV light at wavelengths shorter than 354 nm. PL emission spectra obtained under such conditions are shown in Fig. 3. At 10 K the peak emission occurred at around 2.25 eV. Higher transducer temperatures caused the emission intensity to decrease and the peak emission energy to shift toward slightly higher photon energies. At room temperature the remaining emission intensity amounted to roughly 7.5% of its 10 K value.

In order to achieve sensitivity of the emission characteristics to the H_2 concentration in the ambient air, a semi transparent layer of catalytic Pt was deposited via physical vapor deposition onto

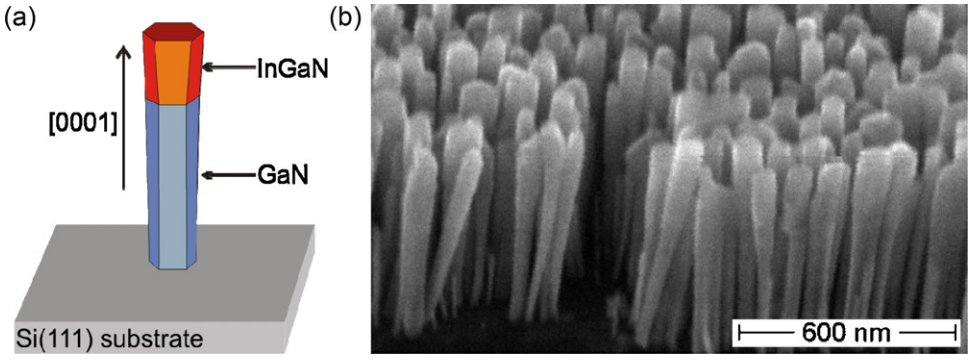

Fig. 2. (a) Schematic of a single nanowire (NW) and (b) SEM micrograph of an array of GaN/InGaN NWs on Si (1 1 1), taken at 45° inclination. The upper InGaN part of the NWs is slightly conically widened.