Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he

Room temperature H_2 sensing using functionalized GaN nanotubes with ultra low activation energy

Prasana Sahoo [a], *S. Dhara* [a,*], *S. Dash* [a], *S. Amirthapandian* [b], *Arun K. Prasad* [a], *A.K. Tyagi* [a]

[a] *Surface and Nanoscience Division, Indira Gandhi Center for Atomic Research, Kalpakkam 603102, India*
[b] *Materials Physics Division, Indira Gandhi Center for Atomic Research, Kalpakkam 603102, India*

ARTICLE INFO

Article history:
Received 3 July 2012
Received in revised form
20 December 2012
Accepted 28 December 2012
Available online 29 January 2013

Keywords:
Gallium nitride
Hydrogen sensor
Platinum functionalization

ABSTRACT

A single-step synthesis route of square shaped wurtzite GaN nanotubes is reported by a quasi-vapor–solid process with detailed growth kinetics involving surface energies and Ga mobility along different crystalline facets. A wet chemical route is used for the functionalization of GaN nanotubes with Pt nanoclusters of average diameter ~1.6 (0.4) nm in order to instigate the formation of localized Schottky barrier, responsible for carrier transport in the sensing process. Catalytically enhanced dissociation of molecular H_2 down to the lowest detection limit of 25 ppm at room temperature, as compared to those of reported GaN systems has been shown. We report, for the first time, a very low activation energy value of 29.4 meV which will be useful in practical sensing of H_2 at room temperature without any application of bias.

1. Introduction

Nanotubes (NTs) with large surface areas and unidirectional curvature have received considerable interest in wide range of applications pertaining to nanofluidics, drug delivery, catalysis, and chemical sensing [1–4]. Direct and wide band gap GaN is one of the most promising semiconductors in future high-power optoelectronic devices and sensor applications [4]. Considerable progress has been achieved toward controlled growth of GaN nanowires and improvising desired functionality by appropriate surface modification. However, there is only a few published work on the growth of amorphous, polycrystalline, and single-crystalline GaN NTs mostly employing template or using metal catalysts [5–13]. In such methods, incomplete removal of template material, partial inclusion of catalyst into the tube annulus and high porosity in as-grown samples are major blocks in the fabrication process of high pure GaN NTs. To date, contamination free direct fabrication of a GaN tubular structures have been a technical challenge. In the present work, an effort has been made to synthesize catalyst free growth of GaN NTs via a quasi vapor–solid (VS) process with an attempt toward elucidation of the underlying growth mechanism.

While looking toward the device performance using nanowires or NTs, the role played by various functional groups in interface with zero-dimensional nanocrystallites assumes enormous importance [4,14–16]. Decoration of compound semiconductors with noble metal nanoclusters like Pd or Pt are of specific interest since these metals act as catalysts for numerous surface chemical reactions. An oxidation step is usually employed specifically to impart photocatalytic H_2 generation capability [17,18], and to produce continuous hot electron flow in nanodiodes [19–22]. In addition, such a step usually enhances electrochemical activity

* *Corresponding author*. Tel.: +91 44 27480500x22513; fax: +91 44 27480081.
E-mail address: dhara@igcar.gov.in (S. Dhara).
0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2012.12.131

[23] and H_2 sensing response across wide range of temperature [24,25]. For example, there were several reports from Somorjai's group on the generation of steady state chemicurrent using a planar nanodiode device which employed 5–8 nm sputtered thin film of Pt over thick GaN film, and also metal-oxide bases [20–22] at times. They have achieved hot electron generation induced chemi-current yield of $(3.5 \pm 0.8) \times 10^{-3}$ under catalytic reaction of O_2 or CO gas. The aforementioned value is found to be one order of magnitude higher than that for Pt/Pd–TiO_2 [21]. There are several reports on Pt catalyzed carbon materials, metal oxides and metal-oxynitrides used in large scale solar energy assisted H_2 production from water [26]. Pt-loaded metal nitride nanoclusters depict superior yield than oxide counterpart toward solar energy assisted H_2 production. However, studies on the metal–semiconductor interface structure and crystallinity are important for its applications in device [27].

In the present study, we have reported a methodology for synthesizing well faceted square shaped high yield GaN NTs with possible growth mechanism. These NTs were covalently functionalized with Pt nanoclusters via a wet chemical route. Room temperature (RT) H_2 sensing with the lowest detection limit, reported so far using GaN system, has been performed on these Pt-decorated NTs with detailed analysis of activation energy of the process.

2. Experimental

2.1. Growth of GaN nanotubes

NTs were synthesized using a hot walled CVD reactor [28–30]. Initially, a Si substrate coated with 3 nm of Au was placed horizontally on the top of a high pure alumina boat (99.95%) at a distance of ~20 mm from the Ga (99.999%, Aldrich) source, which was kept at the upstream side of the same boat. The growth was carried out within the hot zone of the tubular furnace. The furnace tube was initially evacuated to 1 mbar base pressure and subsequently the temperature of the chamber was slowly raised to 500 °C with a ramping rate of ~25 °C per minutes. The system was continuously evacuated for 10 min at 500 °C. The temperature of the system was further increased to 900 °C following a fast ramping rate of ~40 °C per minute while maintaining the same base pressure. After the chamber temperature was raised to 900 °C, the base pressure was slowly increased to 1 atm in 10 min by bleeding high purity NH_3 gas at a flow rate of 10 sccm. The reaction was terminated after duration of 2 h. The system was allowed to cool down slowly to RT in the same NH_3 ambient. A large quantity of light yellowish material was found to be coated uniformly throughout the Si substrate. To identify the growth mechanism of NTs, the role of the most decisive growth parameters, namely, growth rate, temperature and NH_3 partial pressure were taken into consideration.

2.2. Chemical functionalization and metallization

The NTs were further functionalized with Pt nanoclusters using lysine $[HO_2CCH(NH_2)(CH_2)_4NH_2]$ as a capping agent following a standard procedure [31]. Initially, GaN NTs were treated with a diluted piranha solution (50% aqueous solution containing H_2SO_4:H_2O_2: 3:1) for 5 min, and then washed with deionized water (~18 MΩ) followed by a drying process using N_2 gas. The hydroxylated samples were treated with solution containing 1 mM of lysine followed by 1 mM of $HPtCl_4$ in continuous stirring condition for 30 min. A freshly prepared solution of 0.1 M $NaBH_4$ was added slowly into the mixture in order to achieve the desired decoration of Pt nanoclusters surrounding the NTs. The product was washed and dried following the above mentioned process. The Pt coated samples were heated at 300 °C for 30 min to remove lysine [31]. Contact probes were made by sputtering a 5 nm thick Cr followed by 80 nm thick Au films on inter-digitated electrodes with 1 mm spacing for electrical measurements.

2.3. Characterization methodologies

Morphological features of the NTs were examined by field emission scanning electron microscopy (FESEM; Model Zeiss SUPRA 40). High resolution transmission electron microscopy (HRTEM; Libra 200 Zeiss) and selected area electron diffraction (SAED) were employed for structural characterization. Micro-Raman scattering (inVia Renishaw spectrometer) with 514.5 nm line of Ar^+ laser excitation (<1 μm laser spot at the sample surface) using 3000 gr mm^{-1} grating and micro-PL with 325 nm line of He–Cd excitation using 2400 gr mm^{-1} grating assisted with thermoelectric cooled CCD detector in the back scattering configuration were performed for optical characterization of the as-grown sample. A liquid N_2 stage (Linkam) was used for temperature dependent (80–800 K) measurements. In-situ H_2 sensing was carried out by using a custom built in-house gas exposure facility.

3. Results and discussion

3.1. Morphological studies

Fig. 1a–c shows typical FESEM images of the pristine NTs on Si substrate. Highly dense GaN layer of thickness ~20 μm is seen over the Si substrate, as revealed from the tilted cross-sectional image (Fig. 1a). A close view of the magnified image at middle region (Fig. 1b) reveals that NTs are homo-epitaxially grown over a layer of GaN nanoclusters with overall thickness ~2 μm (Fig. 1a). The underlying GaN nanocluster layer may have acted like a buffer layer, which has initiated the NT formation. On mechanical scratching it is found that the as-grown GaN NT layer can be smoothly removed from the nanocluster interface region (Supplementary Information Fig. S1). It is worthwhile mentioning that NTs can be isolated without being contaminated with nanocluster impurity. The surface layer, as observed from the side (Fig. 1c) and normal views (Fig. 1d), reveals that the GaN NTs are homogeneously distributed throughout the surface. The typical images of the Pt decorated GaN NTs are shown in Fig. 1d–g. Most of the NTs exhibit nearly square shaped cross-section (Fig. 1f) with wall thickness of about ~10–15 nm and average side dimensions of nearly ~50 nm (Fig. 1g). Typical length extends to several micrometers.