Materials Letters 79 (2012) 212–215

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Photoluminescence and hydrogen storage properties of gallium nitride hexagonal micro-bricks

Ghulam Nabi [a], Chuanbao Cao [a,*], Sajad Hussain [a], Waheed S. Khan [a], Tariq Mehmood [a], Zahid Usman [a], Zulfiqar Ali [a], Faheem K. Butt [a], Yan Fu [a], Jili Li [a], M. Zubair Iqbal [b]

[a] Research Centre of Materials Science, School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China
[b] Department of Physics, School of Applied Science, University of Science and Technology, Beijing 100083, People's Republic of China

ARTICLE INFO

Article history:
Received 9 January 2012
Accepted 28 March 2012
Available online 4 April 2012

Keywords:
Semiconductors
Defects
Chemical vapor deposition
Hydrogen storage properties

ABSTRACT

A novel morphology of gallium nitride (GaN) hexagonal micro-bricks has been synthesized at 1250 °C by chemical vapor deposition (CVD) method. Photoluminescence (PL) and hydrogen storage capabilities of hexagonal micro-bricks have been investigated. The PL spectrum exhibits strong near-band-edge emission at 369 nm (3.36 eV). Defect related broad yellow band emission at 556 nm (2.23 eV) has also been observed, which plays significant role in the hydrogen absorption. Maximum hydrogen storage capacity of 1.68 wt.% has been achieved under the pressure of 5 MPa and at 373 K. During desorption process under ambient pressure, about 76% releasing of the stored hydrogen has been noted. Highly reversible absorption/desorption results exhibited by GaN hexagonal micro-bricks are encouraging and promising for hydrogen storage.

1. Introduction

Hydrogen is considered as an efficient and clean fuel for the future due to its abundance, easy synthesis, and nonpolluting nature [1]. These significant advantages prefer the use of hydrogen over traditional fossil fuels which pollute the environment, contribute to global warming, and have limited supply. Hydrogen storage plays a key role in the utilization of hydrogen as the energy carrier [2]. In future, usage of hydrogen is very significant as energy source in hydrogen-fueled applications systems and in transportation technologies, such as H_2 fuel cell vehicles [3]. For this purpose an economical and safe nano/microstructure hydrogen-storage medium is critically needed. Up to now, different materials such as Zn_3N_2 [4], Mg_3N_2, AlN, TiN, ZrN [5], BN [6,7], carbon [8], TiS_2 [9], ZnO [10,11] and metal complexes [12] have been studied as hydrogen storage mediums.

GaN is one of the most promising semiconductor materials. GaN has attracted a great attention due to its unique physical and chemical properties like wide band gap ($E_g = 3.4$ eV) at room temperature, high thermal stability and resistance to radiations, high melting point (>2500 °C), high chemical and mechanical stabilities, low electron affinity (2.7–3.3 eV) and high mobility [13,14]. For the synthesis of GaN nano/micro structures different techniques such as sol–gel method [15], sublimation method [16], laser-assisted catalyst growth [17], hydride vapor phase epitaxy [18], molecular beam epitaxy [19], metal-organic chemical vapor deposition [20], and chemical vapor deposition method [13,14] have been used. So far, different properties of GaN such as photoluminescence (PL), electroluminescence, field emission and electronics properties [13–20] have been investigated abundantly. But hydrogen storage properties of GaN have been studied rarely. Only some theoretical investigations have been done by Van de Walle [21], in which it has been revealed that hydrogen acts as an amphoteric impurity in most semiconductors (GaN, AlN) and form hydrogen-impurity complexes. Experimental investigations of the hydrogen storage properties of GaN materials are very exceptional.

In this article we have used simple, facile and low cost catalytic assisted chemical vapor deposition method to synthesize the GaN hexagonal micro-bricks. Hydrogen storage properties of a novel morphology of GaN, hexagonal micro-bricks have been investigated. The effect of hydrogen absorption on PL properties of hexagonal micro-bricks has also been studied. Hydrogen absorption and desorption results examined for GaN hexagonal micro-bricks are very encouraging.

2. Experimental procedure

GaN hexagonal micro-bricks have been synthesized by CVD method from GaN powder locally manufactured from gallium metal in our lab. One gram GaN powder was treated with aqueous ammonia at 150 °C thrice and was loaded in an alumina boat. A cleaned silicon (001) substrate coated with nickel chloride/ethanol solution (0.04 M) was placed on top of alumina boat with a vertical distance 1–2 mm and transferred into horizontal tube furnace (HTF). After sealing the HTF it was heavily flushed with high purity NH_3 gas and its flow was set at 200 sccm (standard cubic centimeter per minute). Subsequently, the furnace was heated at ramp rate of 10 °C/min to reach the maximum set

* Corresponding author. Tel.: +86 1068913792; fax: +86 1068912001.
E-mail address: cbcao@bit.edu.cn (C. Cao).

0167-577X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2012.03.113

temperature of 1250 °C. This maximum temperature was maintained for 3 h. After reaction the furnace was allowed to cool down naturally to room temperature. A thick layer of product collected on the substrate was analyzed.

The structure and the phase purity of the product were determined by X-ray powder diffraction (XRD, Philips X' Pert Pro MPD) and energy dispersive X-ray spectrometer (EDX). The morphologies of the product were examined by scanning electron microscopy (SEM, TM-1000, Japan). The hydrogen storage properties including hydrogen absorption–desorption kinetics were measured by an iso-volumetric method, using a PCT Sieverts-type Gas Reaction Controller. Photoluminescence properties were studied using PL spectrum with Fluorescence Spectrophotometer (F-4500).

3. Results and discussion

3.1. Structural characterization

SEM images of as synthesized GaN micro-bricks have been depicted in Fig. 1. It has been observed that most of the bricks are hexagonal with internal angel 120° and having size of 25–40 μm as shown in Fig. 1 (a,b). The thickness of the bricks has been observed from 10 to 15 μm as shown in Fig. 1 (c). The surface of the bricks is very smooth containing multidimensional particles as publicized in Fig. 1(d). Careful observations of high magnification SEM images showed that most of these particles are hexagonal and some are multidimensional as shown inset of Fig. 1(d).

XRD pattern of the as synthesized GaN micro-bricks has been depicted in Fig. 2. All of the diffraction peaks in the pattern are indexed to wurtzite GaN with lattice parameters a = 3.188 Å and c = 5.187 Å which are in good agreement with the JCPDS card (no. 076-0703). No other peaks of crystalline impurities, such as Ga or

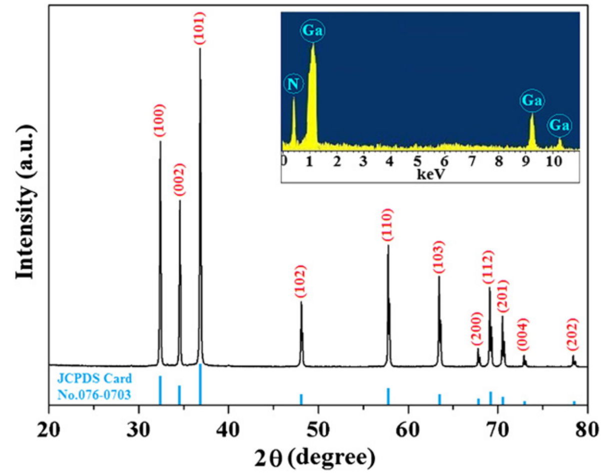

Fig. 2. XRD pattern of the as-synthesized GaN hexagonal micro-bricks (inset is the corresponding EDX).

Ga_2O_3 have been detected within the detection limit which shows that the synthesized product is single phased.

Quantitative analysis has been achieved by EDX of the product as publicized in the inset of Fig. 2. EDX results verify that the product is composed of the Ga and N elements and the weight ratio of Ga/N was about 1:1 within the experimental errors.

A renowned vapor–liquid–solid (VLS) growth mechanism has been proposed for the growth of GaN micro-bricks which has widely been used to interpret the growth of different GaN structures [14]. As we have pre-treated the precursors with aqueous NH_3 which provides the favorable conditions and plays an effective role in the growth of the GaN product [13]. Later when the precursor is heated inside a horizontal

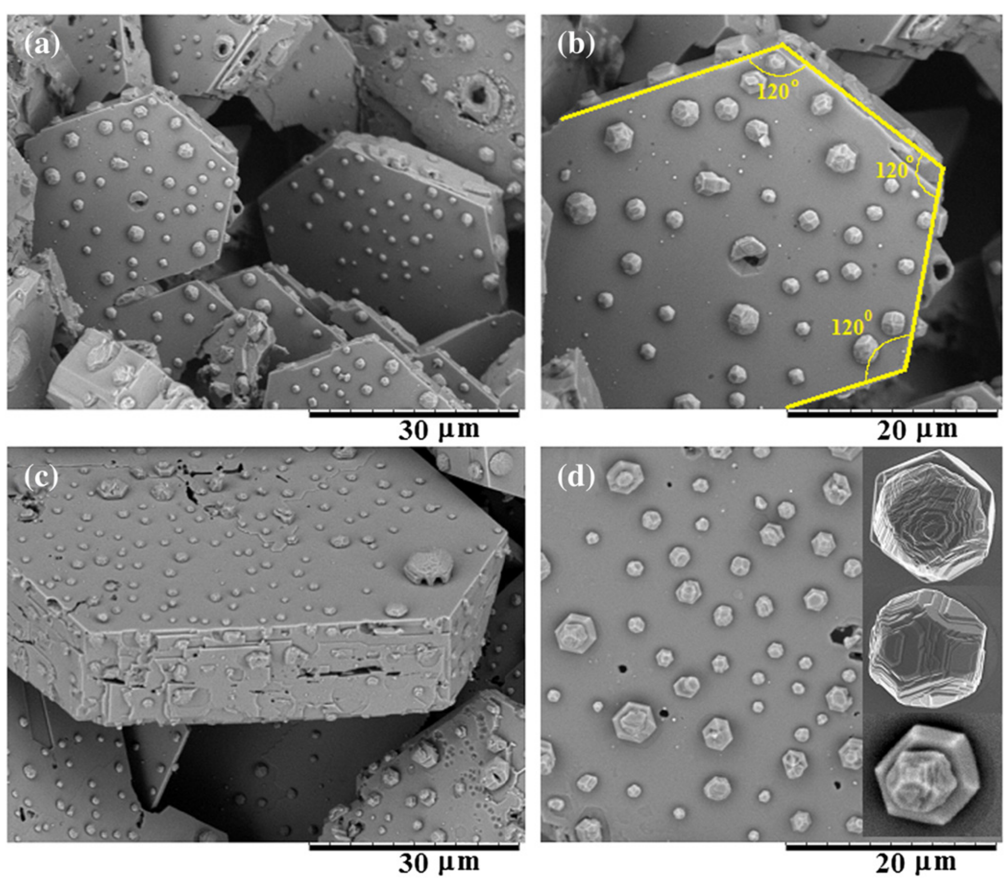

Fig. 1. (a–c) SEM images of GaN hexagonal micro-bricks and (d) surface of the brick (the inset on the right hand side is high magnification of the particles on the bricks).