Materials Research Bulletin 47 (2012) 2277–2281

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Synthesis of vertically aligned boron nitride nanosheets using CVD method

Chao Zhang, Xiaopeng Hao *, Yongzhong Wu *, Miao Du

State Key Laboratory of Crystal Materials, Shandong University, 27 Shandanan Road, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 23 October 2011
Received in revised form 27 April 2012
Accepted 23 May 2012
Available online 6 June 2012

Keywords:
A. Nitrides
B. Vapor deposition
D. Optical properties
D. Luminescence

ABSTRACT

Boron nitride nanosheets (BNNSs) protruding from boron nitride (BN) films were synthesized on silicon substrates by chemical vapor deposition technique from a gas mixture of BCl_3–NH_3–H_2–N_2. Parts of the as-grown nanosheets were vertically aligned on the BN films. The morphology and structure of the synthesized BNNSs were characterized by scanning electron microscopy, transmission electron microscopy, and Fourier transformation infrared spectroscopy. The chemical composition was studied by energy dispersive spectroscopy and X-ray photoelectron spectroscopy. Cathodoluminescence spectra revealed that the product emitted strong UV light with a broad band ranging from 250 to 400 nm. Field-emission characteristic of the product shows a low turn-on field of 6.5 V μm^{-1}.

1. Introduction

Recently, 2D materials have attracted great attention since the appearance of the graphene which has been found to possess excellent quantum transport and mechanical properties [1]. Hexagonal boron nitride is comprised of layered structures as the isoelectric analog of graphite. Compared with graphite carbon, BN has excellent mechanical properties and thermal conductivity and is much more thermally and chemically stable, which makes BN a better candidate for composite materials in hazardous environments [2,3]. Boron nitride is a semiconductor with a wide band gap near 6 eV, in contrast to the semimetallic nature of graphite. Recent researches have revealed that BN is of high promise in application of ultraviolet (UV) light emission devices [4,5]. As the main member of BN nanomaterials, single or few layers of boron nitride have interesting properties and potential applications. Terrones et al. found that BN nanoribbons with zigzag edges can behave as metals, thus exhibiting excellent electron field emission properties [6]. Yu et al. detected that boron nitride nanosheets were superhydrophobicity [5]. Ultrathin BN nanosheets protruding from BN fibers and ultrathin BN nanosheets protruding from Si_3N_4 nanowires had been found to exhibit excellent field emission properties [7,8].

Up to now, several methods have been proposed to obtain graphene analogs of boron nitride, including micromechanical cleavage a bulk BN crystal [9], unwrapping multiwalled BN nanotubes through plasma etching [10], sonication [11,12] of BN particles or using a high-energy electron beam [13,14], solid phase reaction [15] and chemical vapor deposition [16,17]. Vertically aligned boron nitride nanosheets were prepared on silicon substrates from gas mixture of BF_3–N_2–H_2 through microwave plasma chemical vapor deposition (MPCVD) technique previously. Yu et al. proposed that the etchant of F atoms and the electrical field were the main reasons for the formation of vertically aligned BNNSs [5].

In this paper, we report the synthesis of 2D boron nitride nanosheets protruding from BN films on silicon substrates from gas mixture of BCl_3–NH_3–H_2–N_2 by chemical vapor deposition technique. No electrical field was applied. The structure and morphology of the products were systematically investigated by scanning electron microscopy, transmission electron microscopy and Fourier transformation infrared spectroscopy. The chemical composition was studied by energy dispersive spectroscopy and X-ray photoelectron spectroscopy. The optical property of boron nitride nanosheets studied via cathodoluminescence spectra reveals strong cathodoluminescence emission in the ultraviolet range, and this indicates that the present novel BN nanosheets are highly promising for application in optical devices. A turn-on electric field of 6.5 V μm^{-1} has been observed in the as-prepared BN nanosheets.

2. Experimental

The growth of the BNNSs protruding from BN films was performed in a quartz tube type conventional CVD system. A silicon monocrystal wafer as the substrate was placed in the center of the quartz tube. The furnace was first flushed with pure nitrogen gas for 30 min and then the furnace was heated under

* Corresponding authors. Tel.: +86 0531 88366218; fax: +86 0531 88362321.
E-mail addresses: xphao@sdu.edu.cn (X. Hao), wuyz@sdu.edu.cn (Y. Wu).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.05.042

N_2 + 5% H_2 gas (200 ml min^{-1}). When the temperature of the substrate reached 1000 °C, NH_3 and BCl_3 were separately introduced into the tube. The gas flow rates of N_2 + 5% H_2, BCl_3, NH_3 were 200, 15, 150 ml min^{-1}, respectively. After 30 min, the gases BCl_3 and NH_3 were cut off and the furnace cooled down to ambient temperature.

The morphology and structure were examined by a Hitachi S-4800 scan electron microscopy (SEM) and a JEOL JEM-2100 high-resolution transmission electron microscopy (HRTEM) operated at 200 kV. Fourier transform infrared (FTIR) spectroscopic study was carried out on a NEXUS 670 FT-IR. Chemical composition was determined using an energy dispersive spectroscopy (EDS) system attached to S-4800 SEM and an ESCALAB 250 X-ray photoelectron spectroscopy (XPS). A cathodoluminescence (CL) spectrophotometer attached to a SU-70 field emission scan electron microscopy (FE-SEM) was used to investigate optical properties of the synthesized product. The field emission (FE) property of the product was measured in a vacuum chamber, which was pumped down to 10^{-6} Pa by an ultrahigh vacuum system.

3. Results and discussion

The SEM images of the obtained sample are shown in Fig. 1a and b. The substrate surface is homogeneously covered by a thick

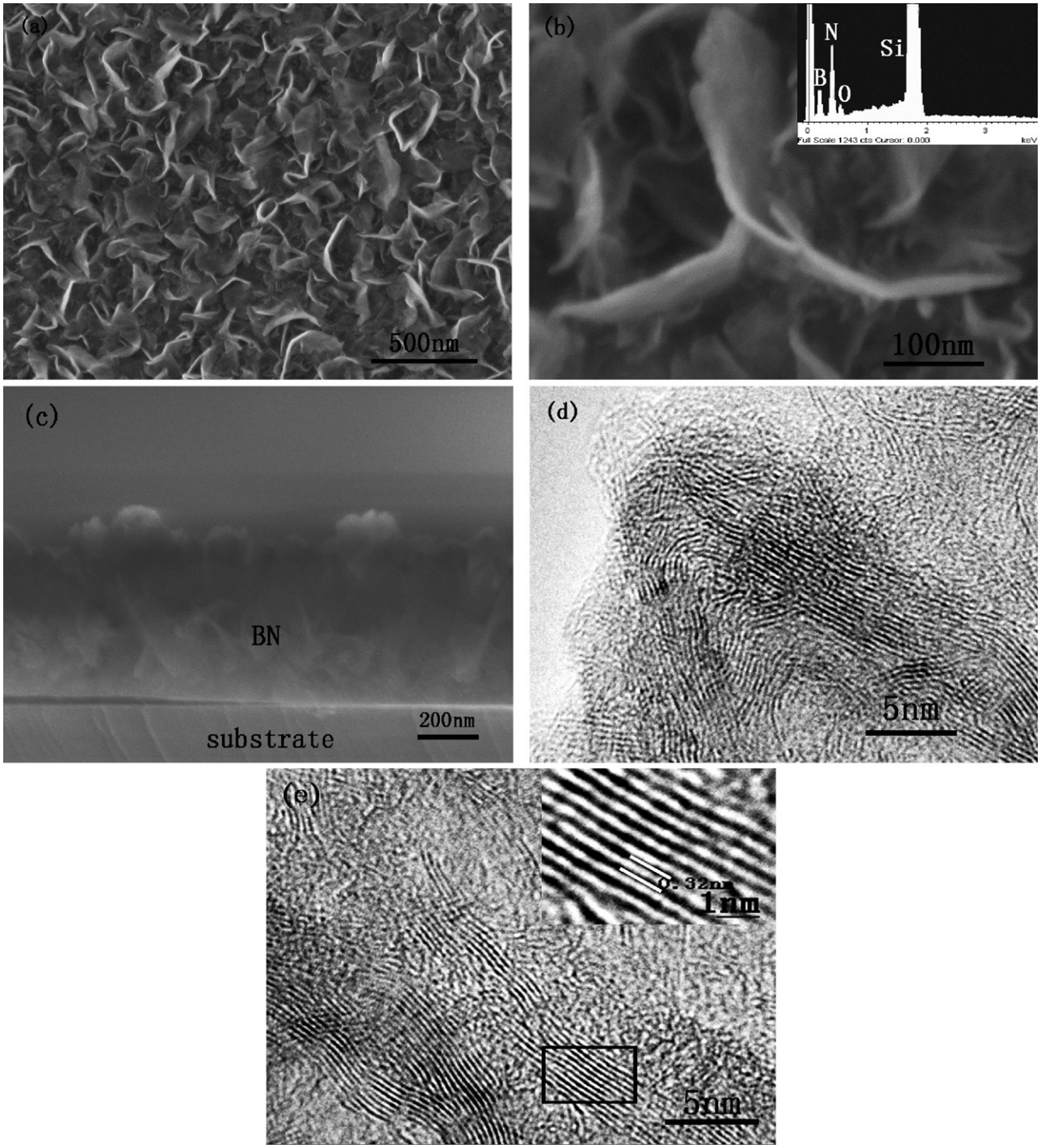

Fig. 1. (a) Low and (b) high magnification SEM images of the product (the inset is the EDS spectrum of the product); (c) section SEM image; (d) and (e) HRTEM images of the product (the inset is the enlarged image of the rectangle domain).