Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 61 (2013) 1266–1273

Acta MATERIALIA

www.elsevier.com/locate/actamat

Nonwetting “white graphene” films

Amir Pakdel *, Xuebin Wang, Yoshio Bando, Dmitri Golberg *

International Centre for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan

Received 18 August 2012; received in revised form 31 October 2012; accepted 1 November 2012
Available online 3 December 2012

Abstract

Nonwetting (superhydrophobicity) is currently of great interest in advanced materials research for self-cleaning applications, although it has been a well-known phenomenon in nature (e.g. in lotus leaves) for a long time. Aiming at widening the potential applications of synthetic superhydrophobic films, we have used a noncatalytic chemical vapor deposition method to prepare superhydrophobic films consisting of boron nitride (BN) nanosheets, also known as “white graphenes”. A mixture of boron (B) and boron trioxide (B_2O_3) powder was used as a new precursor to grow such nano-rough films. The peculiar surface topography of the films induced a nonwetting behavior which was manifested by the picking up of external particles through water droplets rolling on their surface. The nonwetting tendency of the films is explained based on the interactions of the dipole moments of polar water molecules and BN nanosheets.

Keywords: Boron nitride nanosheets; Surface roughness; Dipole moments; Wetting; Self-cleaning

1. Introduction

Nanostructures consisting of a honeycomb network such as carbon nanotubes (CNTs) and graphenes have been in the forefront of materials science due to their unique properties and promising potential applications. A structural analogue of the carbon honeycomb lattice is hexagonal boron nitride (h-BN), in which C atoms are fully substituted with alternating B and N atoms. BN nanostructures exhibit diverse one-dimensional (1-D) and two-dimensional (2-D) morphologies, such as BN nanotubes (BNNTs), nanoribbons (BNNRs) and nanosheets (BNNSs) [1–3]. A hexagonal BN sheet and graphene have nearly identical lattice parameters, but, unlike graphene, BNNSs do not absorb light in the visible region of the electromagnetic spectrum and thus are called “white graphenes”. In contrast to the semimetallic nature of graphite, BN is a semiconductor with a wide band gap of ~6 eV and possesses much higher chemical and thermal stability than its graphitic counterpart [4]. To date, extensive research has been conducted on the synthesis of BNNTs and their properties, suggesting many propitious applications such as gas absorbers, polymeric composites, electrical nanoinsulators, electron field emitters, ultraviolet photodetectors and hydrogen accumulators [4–9]. It is thus expected that other BN nanostructures, such as BNNSs, may also demonstrate interesting properties and find innovative utilizations in various areas.

Highly hydrophobic coatings and films are currently of increasing research interest and a number of methods have been established to produce such nonwetting surfaces [10]. In general, wettability of a surface depends on its chemical composition and microstructural geometry. Nonwetting surfaces with large water contact angles (CAs) can be prepared via two approaches: (1) chemical functionalization of the surface with materials of low surface free energy; (2) creating micro/nanoscale roughness on the surface [11]. Superhydrophobic surfaces exhibit extreme water-repellency, i.e. water droplets resting on them exhibit contact angles larger than 150°. Although water can easily wet the bulk BN surface (i.e. BN surface shows hydrophilicity), the films consisting of BN nanostructures have

---

* Corresponding authors. Tel.: +81 29 860 4696; fax: +81 29 851 6280.
E-mail addresses: PAKDEL.Amir@nims.go.jp (A. Pakdel), GOLBERG.Dmitri@nims.go.jp (D. Golberg).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actamat.2012.11.002

demonstrated ultrahydrophobicity [12–15]. There have been many reports on superhydrophobic films made of organic materials with low surface free energies, such as silicon-based hydrocarbons [16] and fluorinated polymers [17]. Also, several works on surface roughening have been performed, such as making electrodeposited gold cluster films [18], anodic oxidation of aluminum [19], fabricating aligned CNTs [20], producing films of zinc oxide (ZnO) [21] and synthesizing titanium oxide (TiO_2) nanowires [22]. However, unlike BN, most of these materials are not applicable at either high temperatures or harsh environments (e.g. highly acidic or alkaline media).

Recently we have reported the synthesis of BNNS films on silicon/silicon dioxide (Si/SiO_2) substrates by thermal chemical vapor deposition (CVD) of B, magnesium oxide (MgO) and iron oxide (FeO) powder under ammonia (NH_3) gas flow [13]. To investigate the effect of the initial precursor materials on the growth and properties of such films and to increase the activity of the precursors, in this work MgO and FeO were replaced by another oxidant, B_2O_3. The obtained BN films had nano-rough surfaces and exhibited superhydrophobicity and self-cleaning ability. To find clues about the roots of their nonwetting behavior, a density functional theory (DFT) method was utilized. Such water-repelling films are envisaged to find smart applications in surface protection of portable electronic products, non-fogging displays, medical and optical devices and anticorrosive equipments.

2. Experimental details

The crystalline BN nanosheets were grown via a CVD method in a horizontal tubular electric furnace. Elemental B and B_2O_3 powders were mechanically mixed and positioned in an alumina combustion boat covered with a Si/SiO_2 substrate. The boat was then set into a quartz test tube inside a vacuum chamber. The chamber was evacuated to ∼1 torr and then ammonia gas was introduced at the rate of 0.4 ml min^{-1}. The precursors were heated to 1200 °C, held for 60 min and then cooled to room temperature.

The morphology and chemical composition of the films were studied by a field emission scanning electron microscope (FE-SEM; Hitachi S4800) equipped with an energy dispersive X-ray spectrometer (EDX). Structural features of the nanosheets were investigated by a high-resolution field-emission transmission electron microscope (HRTEM; JEOL JEM-2100F) equipped with an electron energy loss spectroscopy (EELS) detector. The topographical images of the films were obtained by a JEOL JSPM-5200 scanning probe microscope in the tapping atomic force microscopy (AFM) mode at ambient conditions. The water contact angle (CA) measurements were carried out by a sessile drop method using deionized water droplets of ∼8 to 16 μl volume positioned on the films using a microsyringe. A high resolution Keyence VH-5000 optical instrument equipped with WinROOF V5.03 analysis software was used for measuring the water CA.

To compare the dipole moments of perfect and wrinkled BN surfaces, electronic structure calculations were performed within the context of density functional theory (DFT), using the Perdew–Burke–Ernzerhof [23], exchange–correlation functional and projected augmented wave methods, as implemented in the VASP code [24]. In all calculations, the corresponding Brillouin zone was sampled by a $4 \times 4 \times 1$ Monkhorst–Pack mesh [25].

3. Results and discussion

Fig. 1a and b displays SEM images of a typical film covering a large area. The nanosheets are uniformly distributed, well-separated and tend to be vertically aligned. The compact morphology of the present BNNSs is similar to that of nanosheets previously prepared by us [13], where a mixture of B, FeO and MgO powders was used as the initial precursor. Although the aforementioned mixture has been found to be an effective source for the growth of BN nanostructures, the formation of $Mg_2B_2O_5$ during the synthesis can reduce the chemical activity of the precursor and consequently hinder the growth of BN nanomaterials [26]. Thus, it is worth finding substitute compounds for precursor materials. Fig. 1a and b indicates that B_2O_3 could be considered as an alternative to MgO and FeO. This suggests that the growth of BNNSs is not strongly dependent on specific precursor materials, as long as enough reactive B and N atoms are provided in the growth atmosphere. Fig. 1c illustrates our suggested model for the two-stage growth of the present BNNSs. After nucleation and primary growth of preferential crystal planes with high growth rate on the substrate, a BN layer could form. Then, at the boundaries between neighboring sheets, top atomic layers could curl up due to the existence of force between them and vertical growth initiated. At last, these thin walls of BNNSs grew taller and formed the peculiar nano-rough morphology of the film.

The BNNSs were characterized by TEM as shown in Fig. 2a and b. The low magnification TEM image in Fig. 2a displays bent and scrolled nanosheets, as was anticipated as an intrinsic feature in 2-D nanostructures. The dark sections in Fig. 2b are the cross-sections of the BNNSs folded back and imaged edge-on. The observed transparency of the nanosheets to the electron beam indicates that they are atomically thin. The HRTEM image in Fig. 2b shows highly ordered lattice fringes, indicating that the BNNSs are well-crystallized. The average distance between adjacent fringes is ∼0.33 nm, signifying that the regarded lattice fringes correspond to (002) crystal planes of h-BN. Curled edges of nanosheets made it possible to evaluate the sheet thicknesses from the HRTEM images. Having checked several sections in different HRTEM images, it was concluded that the majority of the BNNSs were less than 5 nm in thickness.