Microelectronic Engineering 126 (2014) 124–128

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Electric field used as the substitute for ultrasounds in the liquid exfoliation of hexagonal boron nitride

A. Sokołowska [a], J. Rudnicki [a], M. Kostecki [a,*], S. Wojtkiewicz [b], P. Sawosz [b], R. Chodun [a], K. Zdunek [a], A. Olszyna [a]

[a] Warsaw University of Technology, Faculty of Material Science and Engineering, 141 Woloska Street, 02-507 Warsaw, Poland
[b] Nalecz Institute of Biocybernetics and Biomedical Engineering, Polish Academy of Sciences, 4 Trojdena Street, 02-109 Warsaw, Poland

ARTICLE INFO

Article history:
Received 27 September 2013
Received in revised form 29 April 2014
Accepted 27 June 2014
Available online 11 July 2014

Keywords:
Boron nitride
Nanosheets
Liquid exfoliation
Electric field

ABSTRACT

Nanosheets of hexagonal boron nitride (hBN), several nanometers thick, were produced by liquid exfoliation in polar liquids with the assistance of an electric field (f = 40 Hz, E = 7 mV/μm). The use of ethylene glycol eliminated the aggregation of the nanoparticles. The electric-field-enhanced liquid exfoliation appeared to be an energy-saving process compared to sonication (10^3 times better in this respect). This benefit can be attributed to the fact that here the electric energy is only consumed by the interactions between the atoms located on the crystal planes; that is, it is only involved in the exfoliation process, whereas in sonication the energy is engaged in the whole collision process.

1. Introduction

The technology employed for the manufacture of 2D nanomaterials (nanosheets) by the liquid exfoliation of layered crystals is inexpensive and effective [1–4]. This method allows to produce nanosheets without defects, which cannot be obtained by using other techniques, e.g. CVD. This is particularly important for applications in electronics. The process has a synergic character; that is, the action of the liquid adhesion forces must be supported by additional thermodynamic stimuli – usually ultrasound or milling, at present.

The aim of our study was to examine experimentally whether the electric energy affects the liquid exfoliation of layered dielectric crystals, assuming that the electric field acts as the additional thermodynamic stimulus which alters the energy state of the material through, for example, its polarization. According to our knowledge, no reports on experimental studies of electric-energy-enhanced liquid exfoliation have yet been published.

The layered crystals have a strongly anisotropic structure composed of flat planes in which the atoms are bonded by covalent or covalent-ionic bonds joined by weak van der Vaals forces. In dielectric layered crystals which are chemical compounds (BN, oxides and sulfides of transition metals, etc.), the bonds are covalent-ionic and thus we can expect polarization effects to occur when the crystal is placed in an external electric field. If this is so, dipole forces will appear, which will enhance the action of the liquid adhesion-induced exfoliation forces. The authors of Ref. [5] analyzed theoretically the impact of an electric field on the exfoliation of dielectrics in terms of energetics. They express the free energy of a plate as a function of the plate shape (length-to-thickness ratio, l/t), the ratio of the dielectric constants of the plate and the liquid, ε_p and ε_m, respectively, the intensity of the electric field E, and the position of the plate with respect to this field (angle θ). The change in the free energy of the plate due to exfoliation must exceed the interfacial energy E_w. The repulsion is at a maximum at $\theta = \Pi/2$. Hence the critical electric field E_c is found by $E_c^2 = 4E_w/\varepsilon_m t \cdot \text{const}(\varepsilon_p/\varepsilon_m)$.

The estimated value of the electric field necessary to enhance the exfoliation calculated using this formula was $E > 1$–10 V/μm. However the electric field may also have an influence on the nanosheets obtained. Depending on their orientation with respect to the direction of E, the nanosheets may undergo agglomeration or repulsion. The polarizability and alignment of dielectric nanoparticles in an electric field were analyzed theoretically in Ref. [6] for various nanoparticle shapes with the atoms arranged on a simple cubic lattice. The authors of Ref. [6] found that in the case of thin plates the inter-atomic interactions reduce the polarizability in the direction perpendicular to the surface of the plate (along their thickness). Linear assemblies of BN nanosheets in polysiloxane composite [7] and polyester/oriented-graphene composites [8] were fabricated under a DC electric field.

* Corresponding author. Tel.: +48 22 234 74 49; fax: +48 22 234 71 34.
E-mail address: mkostecki@meil.pw.edu.pl (M. Kostecki).

http://dx.doi.org/10.1016/j.mee.2014.06.025
0167-9317/

The effect of electric energy on the exfoliation has been examined experimentally in graphite, which is not a dielectric. The electric-field-assisted exfoliation of highly oriented pyrolitic graphite (HOPG) was examined experimentally by the authors of ref [9,10]. They transferred few-layer graphene nanosheets from pre-patterned pristine HOPG to a substrate (mostly SiO_2) using an electrostatic field of 1.7 MV/cm for a very short time. Graphene nanosheets were also obtained by d.c. electrolysis conducted in ionic liquids [11–14] and in sulfuric acid [15]. Fully expanded graphite at the cathode and fully oxidized graphite at the anode were acquired. The Authors suggested that the electric current acted as the oxidizing and reducing agent [13–15] and the applied voltage aided the intercalation [13] and the expansion of graphitic electrodes [12,13].

In the present study we experimented with the liquid exfoliation of a powder of the hexagonal BN form (hBN). At present, nanosheets of hBN are used as a constituent of composites with the aim of improving their mechanical and tribological properties and increasing their heat conduction [16]. Prospectively, they may find application in electronics as an exceptional insulator in systems with graphene [17,18] and as the basic component of heat transfer fluids [19]. Nanosheets of hBN were obtained by the liquid exfoliation of crystals enhanced by sonication conducted in NN-dimethylformamide [16], isopropylalcohol [2], H_2O [20] and with functionalized hBN – in H_2O and in tetrahydrofuran [21]. Nanosheets were also obtained by liquid exfoliation enhanced by milling [22].

hBN is a layered crystal, isoelectronic to graphite. It is a dielectric with a wide band gap and direct or indirect transitions from 4.47 eV to 6.9 eV [23]. The intralayer chemical bonds have a strong σ sp2 character and in addition a charge transfer between B and N which gives them partially ionic character. The ionic component of the bonds fortify interlayer interactions [24]. Because of this stronger interlayer bonding, the mono-layer sheets of hBN are more difficult to isolate than those of graphene [22].

The effect of the external electric field on the energy state of hBN can be illustrated by the dependence of its absorption of light on polarization. If the light is polarized perpendicularly to the interlayer, the Π–Π^* transitions are dipole-forbidden. This means that the external electric field polarizes the charge distribution in the interlayer, creating a layer of dipoles. It leads to an induced electric field, directed opposite to the external field [23,25].

In our earlier mini-review [4] we strongly emphasized that the liquid exfoliation process is synergic. Based on this feature of the process, we supposed that the external electric field which would be superposed on the interlayer dipole field would function as the additional thermodynamic stimulus, thereby enhancing the exfoliation forces of the liquid adhesion similarly to the case with the mechanical forces which are active in sonication.

Herein we have shown that electric energy can give an enhancement of the liquid exfoliation of the hBN crystals equal to that produced by sonication, and the energetic efficiency of the electric-field-assisted process is higher.

2. Materials and methods

The hBN powder was delivered by the Fluka Chemie GmbH and the remaining reagents by the POCH Company. A microscopic image of the powder is shown in Fig. 1. For the sake of comparison, the powder was subjected to exfoliation enhanced by ultrasound in a sonic bath (Inter Sonic 250 Hz, 300 W) for 1 h. To examine the effect of the electric field, the powder mixed with the liquid was subjected to the action of the electric field for 8 h. The electric field was induced by an a.c. electric current with a frequency of 50 Hz and voltage of 220 V and applied between electrically insulated

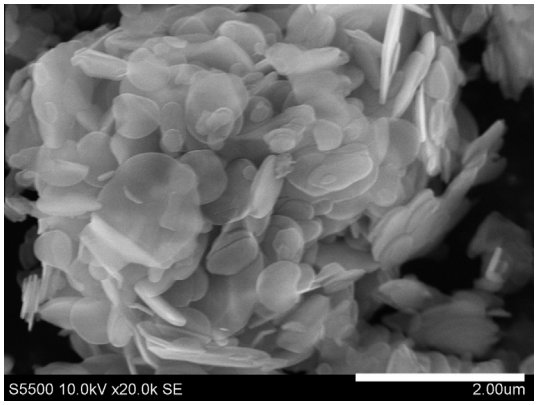

Fig. 1. SEM image of the starting hBN powder.

electrodes spaced at $L = 30$ mm. The suspensions obtained were left to sediment freely so as to avoid additional effects of centrifuging. The samples intended for examination of the nanosheets were taken from the lyosol after 1 day (24 h) to 100 days.

The nanosheets from all the lyosols were visualized in a Hitachi S 5500 SEM/STEM. The samples were prepared by drying droplets of the lyosol on the microscope grid or on a silicon wafer.

Selected lyosols were investigated with the use of the multi-angle static light scattering method described in Ref. [26] to compare the size of the nanosheets formed in the lyosols. The nanoparticles in the shape of plates scatter light in a specific way, so a special method was developed to take into account the effect of the particle shape on the indicatrix of the scattered light. In the method a mathematical model of light scattering by a volume was approximated by a set of small cubical sub-volumes, the Discrete Dipole Approximation [27,28]. One of the implementations of the model, namely the Amsterdam Discrete Dipole Approximation code [29], provides the way to calculate the scattering indicatrix for particles of the presumed shape. In order to characterize the nanoparticles present in a given lyosol, the experimentally measured indicatrix is compared with the one calculated analytically.

In the case of lyosols whose particles we were sure had similar shapes, the scattered light intensities were compared and the difference between the concentrations of nanosheets in the individual lyosols was found using the Rayleigh equation.

In view of the absorption edge of BN, which is $h\nu > 4$ eV, examination of the scattered light is especially advantageous here.

Selected nanosheets were examined by Raman spectroscopy. We studied the Raman scattering using two different excitation energies: 4.66 eV (266 nm) for UV excitation and 2.33 eV (532 nm) for visible. For UV excitation the Crylas FQCW266-50 system was used, employing a 1064 nm line of Nd:YVO4 laser converted to 266 nm in the fourth harmonic generator. For visible excitation, we used the Ar^+ laser. The scattered light was dispersed by a JASCO NRS 5100 spectrometer working in backscattering mode. In each case the laser beams were focused onto spots 10 μm in diameter. In the case of specimen surface measurements, the spectra were measured inside a 7×7 matrix of 15 μm in diameter spots. The spectral resolution of measurements was 1.44 cm^{-1} for UV scattering and 0.62 cm^{-1} for visible scattering.

3. Results and discussion

The nanoparticles obtained by the exfoliation in H_2O, C_2H_5OH, $(CH_3)_2CO$, and $C_2H_4(OH)_2$ enhanced by ultrasound (for 1 h) and an electric field (for 8 h) were compared. The surface tensions of hBN and the liquids are given in Table 1.