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Plasma surface functionalization of boron nitride nano-sheets

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ABSTRACT

On silicon substrates, boron nitride nanosheets (BNNS) consisting of interconnected hexagonal boron nitride nano-layers were produced via chemical vapor deposition process at 1200 °C whose roughness's are at the micrometer- and nanometer-scale. The BNNS were functionalized in argon plasma admixed with ammonia or nitrogen or oxygen. The samples were characterized to investigate the surface chemistry and structural changes after plasma treatment using X-ray photoelectron spectroscope and Micro-Raman spectroscope techniques, respectively. While no significant changes in the surface features, upon plasma treatments of the BNNS, were noticed during SEM and TEM examination, the oxygen functional groups, however, were found to have been incorporated in varying amounts depending on the plasma type. As compared to untreated BNNS, the plasma functionalization treatments made BNNS less hydrophobic. The wettability of the nanostructures, as measured form the water contact angle measurements, is discussed by referring to changes in surface chemistry after plasma treatment.

1. Introduction

Boron nitride nanosheets (BNNS) are boron nitride (BN) based materials consisting of stacked hexagonal BN layers that are assembled in sheets with high aspect ratio and standing vertically on the substrate [1–4]. Recently, these two-dimensional (2D) nanostructures have attracted attention because they exhibit many fascinating properties for advanced applications including, excellent thermal conductivity, high thermal stability as well as supreme mechanical strength [5–10]. These outstanding properties make them potential candidates for smart coatings and optical devices, and in particular, for bio-sensing, microfluidic, catalysis and sequencing filtration for sieving hydrogen isotopes [11–16]. In this context, the surface structure and composition of BN nanostructures considerably influence their physical and chemical properties [6–8]. Although surface functionalization of the BN nanostructures is critical for tuning their characteristics, the studies exploring this research topic are scarce. Pakdel et al. [7] reported surface modification of the BNNS through an air-plasma treatment in order to control their wetting properties. Sainsbury et al. [8] also reported the oxygen radical functionalization of BNNS with the aim of preparing polymer nanocomposite. Other studies reported a monotonic narrowing in the h-BN band gap upon treatment with oxygen plasma due to oxygen dopants incorporation [17,18], whereas hydrogen plasma treatment of few-layer rippled h-BN membranes was found to induce a shift from insulator to semiconductor through reduction in the bandgap value from 5.6 to 4.25 eV [19]..

In this work, the BNNS functionalization was accomplished by means of low-pressure plasmas generated by electrical discharges in argon/ammonia, argon/nitrogen and argon/oxygen gas mixtures. The plasma treatments under controlled conditions preserved the nano/micro features of the BNNS surface, while incorporation of various chemical groups was different for different gas mixtures. The surface chemistry of the samples was assessed by X-ray photoelectron spectroscopy which is a powerful surface characterization technique allowing detailed investigation of the chemical bonding. As compared to the initial BNNS, wettability of the modified surfaces is affected by

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plasma treatments. The results are analyzed in context with wettability and surface chemistry properties of other plasma-modified BNNS.

2. Experimental procedure

2.1. Boron nitride nanosheets (BNNS) synthesis

The Si/SiO_2 substrates were placed over an alumina combustion boat loaded with 20 mg of precursor powder (B:MgO:FeO in a 3:1:1 M ratio). This setup was loaded inside a closed-end quartz tube, and the whole setting was positioned in a horizontal tube furnace with the substrates facing upward. The precursor and substrate were then heated up to 1200 °C with an ammonia (NH_3) flow of 200 sccm for 15 min.

2.2. Plasma-functionalization

The functionalization of BNNS surfaces was performed with low pressure plasmas generated in Ar/NH_3, Ar/N_2 and Ar/O_2 gas mixtures at fixed flow ratio, as described elsewhere [20]. The samples were placed on the grounded electrode of a parallel-plate RF discharge. The functionalization conditions used in the present experiments were as follows: Ar to gas (NH_3, N_2 or O_2) flow ratio (in sccm) 10:25, pressure ≈ 10–20 Pa, RF power 20 W and treatment time 10 min. The samples were treated with Ar/NH_3, Ar/N_2 and Ar/O_2 plasmas with fixed flow ratio.

2.3. Materials characterization

The samples were characterized under scanning electron microscope (SEM; JEOL JSM 7600F) and transmission electron microscope (TEM; H9000-NAR, Hitachi). For TEM examination, the specimens were prepared by scratching the plasma-treated samples with a diamond tip and collecting the debris over a TEM copper grid covered with a thin holey carbon film. The TEM was operated at an accelerating voltage of 300 keV. Although the operating voltage is greater than the knock-on damage threshold of 74 and 84 keV for the B and N atoms, respectively [21] the BNNS were examined for very brief times and at reduced illumination to avoid any knock-on damage to the nanosheets. This approach has been reported to be quite effective in many earlier works [22,23].

The Raman spectra were recorded using Jobin-Yvon LabRAM HR800 spectrometer with a HeCd Laser (λ = 325 nm). For surface analysis, XPS measurements were carried out on a Kratos Axis Ultra using AlKα (1486.6 eV) radiation. High resolution spectra were acquired at 20 eV pass energy. The C 1s line of 284.4 eV was used as a reference to correct the binding energies for charge energy shift. A Shirley background was subtracted from the spectra and signals and the symmetric Gaussian functions were used during peak fitting procedure. The condensation experiments and contact angle measurements were made to determine wettability. The contact angle measurements were performed using a KSV CAM101 instrument consisting of a single compact unit equipped with FireWire video camera of 640 × 480 pixels resolution, a test stand, a standard syringe and an LED source. The contact angles were measured using a wetting liquid. The experiments were performed at room temperature by placing a drop of about 1 μL of distillate water on the surface.

3. Results and discussion

The surface morphology of the as-deposited BNNS was examined under SEM, as presented in Fig. 1. The BNNS are noticed to exhibit bending and crumpling during growth. The nanosheets deposition on Si substrate can be explained by the theory of BNNS nucleation and subsequent growth [24,25]. The surface microstructures at low and high magnification represent 2D interconnected nanosheets with their edges tilted or oriented perpendicular to the substrate. The BNNS appear to be irregularly shaped with lateral surface area of the order of few hundred square nanometers. Upon plasma treatment, there was no apparent change in the surface morphology of the BNNS modifications when compared with SEM results of the as-synthesized samples (not shown here).

In order to better elucidate the as-synthesized BNNS for thickness and surface features, TEM studies were performed, as shown in Fig. 2. The low magnification TEM microstructure in Fig. 2a shows BNNS with bending and scrolling morphology at or near their edges. This structure is commonly observed in 2D nanostructures and was also reported in case of carbon nanowalls [26]. The selected area electron diffraction (SAED) pattern (inset of Fig. 2a) shows two diffraction rings, (002) and (100), characteristic of the layered BN related to h-BN. High-resolution TEM (HRTEM) images, from regions B and C of Fig. 2a (Fig. 2b, c) show highly ordered lattice fringes, indicating that the BNNS are crystalline. The measurements on many nano-sheets (inset of Fig. 2b) revealed the spacing between adjacent fringes to be ~0.34 nm, which is close to the (002) inter-planar distance of h-BN [2–4,7]. Moreover, the HRTEM image in Fig. 2b reveals closed edges with bending structure of many layers, with some discontinuity and distortion. The Fig. 2c reveals an open, sharp-ending knife-edge feature comprising of few layers. From electron microscopy and SAED pattern, it can be deduced that the BNNS produced under the processing conditions of this study are polycrystalline and exhibit a range of thickness values, thus comprising of few to many layers. Although the operating voltage (300 keV) was in excess of the knock-on damage threshold for ultrathin BNNS, precautions observed during electron microscopy and the fact that a significant fraction of the BNNS had thickness on the order of few nanometers, implies that there was no damage in the BNNS structure during TEM examination. Due to their high surface area, flexibility, thermal, and chemical stability, these BNNS are promising nanostructures for catalysis and sensing applications [1–6].

Raman spectroscopy is generally considered a sensitive tool for identification of the BN nanostructures. Raman spectra of the BNNS samples, before and after plasma treatment, were measured, as shown in Fig. 3. The as-synthesized and Ar/NH_3 plasma-treated BNNS samples exhibit a peak at 1367 cm^{-1} which can be attributed to B—N high frequency vibration mode (E_{2g}) in h-BN [2,3]. The crystalline quality of the BN materials can be evaluated by the relative position and full-width-half-maximum (FWHM) values of the Raman peaks [2,3,27,28]. Furthermore, Nemanich et al. [29] showed that both position and FWHM for the high frequency E_{2g} mode vary inversely with crystallite size (base-plane dimension). In our case, since all the BNNS samples were deposited under identical processing conditions, any shift related to the difference in crystalline size can be ruled out.

In case of Ar/N_2 and Ar/O_2 plasma-treated BNNS samples, the peak related to E_{2g} mode is blue shifted by almost 0.9 cm^{-1} with respect to those of both as-made and the Ar/NH_3 plasma-treated BNNS. This upshift of E_{2g} may be caused by high magnitude of in-plane strain and lower interlayer interaction, both of which lead to phonon softening [3,27,28]. This is more probably related to multiple factors including structural disordering or amorphization, oxygen doping and/or adsorption [30,31].

In addition, the FWHM of the Raman peaks related to samples treated in N_2 and O_2 plasma were broadened compared to untreated and NH_3 plasma treated samples. The FWHM values of the latter were estimated to be 22.35 and 21.50 cm^{-1} (for as-synthesized and Ar/NH_3 plasma treated BNNS, respectively). For Ar/N_2 and Ar/O_2 plasma treated BNNS, the relatively higher FWHM values of 24.8 and 25.4 cm^{-1} were recorded. The greater degree of G band broadening is related to oxygen doping and adsorption to the BNNS in predominantly mono- and bi-layer BN. From Raman analysis, it can be deduced that the plasma treatment of the BNNS in N_2 and O_2 plasmas have stronger influence on the BNNS surface chemistry and crystalline quality.

In order to investigate the surface chemistry of BNNS after plasma treatment, XPS analyses were performed on as-prepared and plasma-