Structural Changes of BN Nanotubes Irradiated by Al Ions

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Boron nitride nanotubes (BNNT) have many potential applications as structural and reinforcing materials due to attractive combination of their excellent mechanical characteristics and high thermal and chemical stabilities. Recent progress in their reliable synthesis opened a way to pioneering experiments in BNNT/metal composite fabrication. In this work we have prepared BNNT/Al nanocomposites using the method of ion implantation. Using high-resolution transmission electron microscopy and Raman spectroscopy we have confirmed the formation of hybrid BNNT/Al nanostructures with a partial modification of nanotubes depending on the parameters of ion implantation process. Obtained nanohybrids are envisaged to be an interesting playground for the investigation of processes occurring on the aluminum-BNNT interface.

Keywords: Boron Nitride Nanotubes, Nanotubes/Metal Composites, Mechanical Properties, Structural Changes.

1. INTRODUCTION

Nowadays the majority of structural materials used in automotive and aerospace applications are the low density, light-weight metals and alloys, typically based on aluminum. The components light weight is a key for economic usage of fuel, saving energy and minimization of environment pollution. However, such materials are relatively soft and have a modest ultimate tensile strength (typically around 100–300 Mpa), that further decreases 3–4 times under heating under rather moderate temperatures of 200–300 °C. Making these metallic parts tougher and stiffer should result in a significant minimization of dimensions of structural components, and in a further decrease the overall construction weights. We propose to use multiwalled boron nitride nanotubes for reinforcement of such materials. Aiming at this final goal, and being at the initial stage of its accomplishment, in this article we present the initial results on BNNT/Al nanocomposites preparation and characterization.

Excellent mechanical properties of BNNTs, their high thermal and chemical stabilities, heat resistance and

thermal conductivity[1] make them an ideal candidate for application in composites. Last years the experimental investigations of individual BNNT mechanical properties have been carried out with a special *in-situ* transmission electron microscopy technique.[2–4] These experiments have revealed BNNT superstrong performance, such as superb resistivity to high tensile and bending stresses, unique elasticity and excellent resilience to cyclic deformations.

The method of ion implantation is widely used for modification of surfaces and internal structures of various materials. Recently this method has been employed by several groups for the nanomaterial property tailoring. These works are mainly devoted to modification of chemical, mechanical, electronic and optical properties of carbon nanotubes for needs of technological applications.[5–8] Meanwhile the non-carbon nanostructures attracted less attention. Only a few works devoted to TiO_2 and BN nanotubes modification with light ions (as nitrogen, argon and helium) have been published.[9, 10] Until recently there were almost no efforts to prepare BN nanotube/metal composites using ion implantation of metals. In our previous work[11] we have studied multiwalled BNNT modification by metal ion implantation in various conditions. Here,

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based on these first results, we have focused on preparation of BNNT/Al nanocomposites. We intend to obtain BN nanotubes covered by an Al layer. Such material is expected to become a convenient system for investigation of mechanical properties of BNNT-reinforced metals. It is also supposed to be a convenient system for a comprehensive investigation of metal-BNNT interfaces.

2. EXPERIMENTAL DETAILS

Multiwalled BN nanotubes synthesized with so-called boron oxide-assisted chemical vapor deposition (CVD) method were used for experiments. The purified samples were prepared as described in our previous works.[1, 2, 12] For the metal ion implantation experiments and for the following analysis, the BN nanotube samples were prepared via deposition of nanotubes ultrasonicated in isopropanol (~ 0.1 μg/ml concentration) onto copper TEM grids covered with amorphous carbon. The obtained samples were placed in a vacuum chamber in front of the implanter, at a 100 mm distance from the ion acceleration zone (as schematically shown in Fig. 1).

In the first experiments, a wide range of experimental parameters and different standard cathodes (Ni, Ti and Al) were used to determine the preferential implantation conditions.[11] For further experiments, the acceleration voltage of 10–20 kV and the ion current of 10 mA were chosen. At these conditions the homogeneous Al-BNNT nanocomposites were prepared.

Structural changes of the BN nanotubes were studied by a high-resolution transmission electron microscopy and a Raman spectroscopy. Direct observations of the crystalline structures were performed on a JEOL 3100FEF field emission transmission electron microscope operated at 300 kV and equipped with an Omega Filter and an EDX detector. The samples were also characterized using a Jobin Yvon S 3000 Raman spectrometer equipped with 514.5 nm Ar$^+$ laser for excitation. The excitation laser intensity was adjusted before each measurement to avoid heating or thermal modification of the samples.
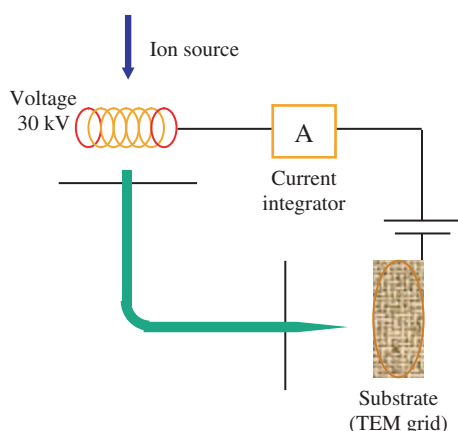

Fig. 1. Scheme of the high energy ion modification experimental setup.

3. RESULTS AND DISCUSSION

Typical transmission electron microscopy images of pristine and Al-ion implanted BNNTs are shown in Figure 2. As-received boron nitride nanotubes (Fig. 2(a)) exhibit specific and well-detectable structures. Usually they are straight, 50–100 nm thick hollow cylinders with the walls consisting of multiple parallel BN shells.

After modification, the overall structure of the nanoobjects changed dramatically. Depending on the nanotube position relative to the ion beam the various structural modifications were observed. Different parts of the sample were not modified uniformly due to the screening effect. Only the nanotubes located in the lower layers of the samples were influenced by the metal ion flow while the nanotubes from the upper parts of the samples were intact. In the modified parts of the samples uniform fibers were observed.
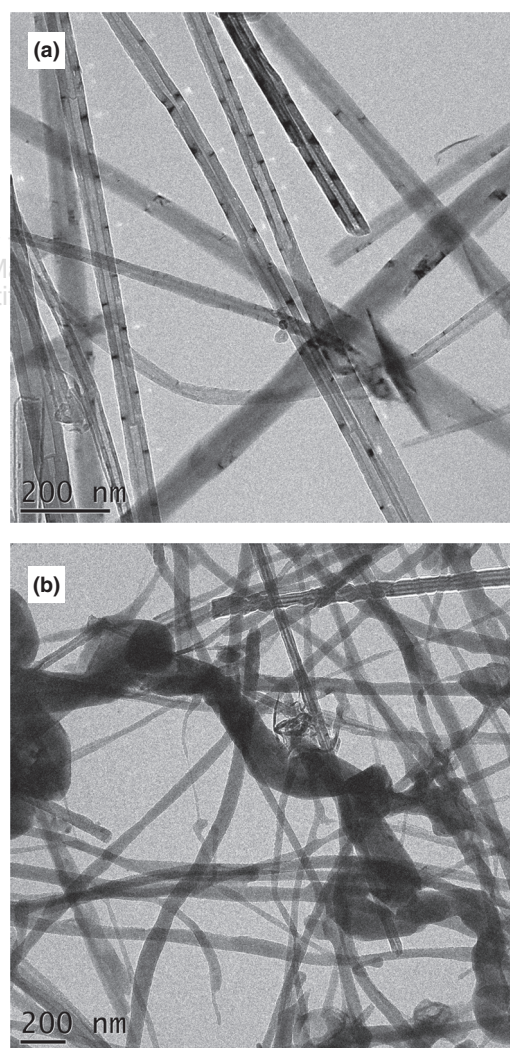

Fig. 2. The overview of the upper (a) and lower (b) parts of BN nanotube sample after its modification with Al ion implantation at 20 kV and 10 mA.

The inner structure of these fibers was analyzed with a high-resolution TEM (Fig. 3). A row of various BNNT modifications were observed. In case of a comparatively low-energy modification the overall BNNT structure was not perturbed. The inner channel and the multiple shells
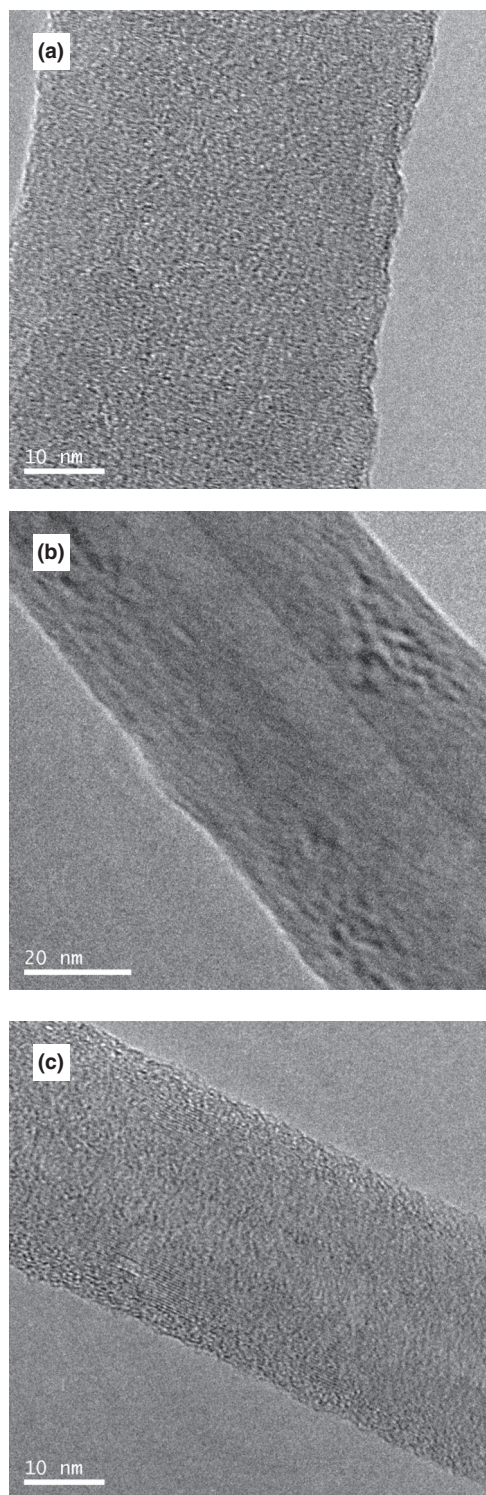
were still clearly seen in Figure 3(a). However, after implantation, the outer shells of nanotubes (being initially straight) were partially amorphized due to penetration of Al ions. During the metal implantation the numerous nanotube areas under stresses have been introduced. They are seen as the dark-contrast areas in TEM images (Fig. 3(b)). In the areas exposed to higher-energy ions, the contrast of structures observed was much darker compared with the previous case. The increased scattering of electrons in these objects confirmed that Al ions were incorporated into the nanotube. A representative example of the intermediate stage of the nanotube modification is shown in Figure 3(c). In this case the nanotube walls were still clearly seen,
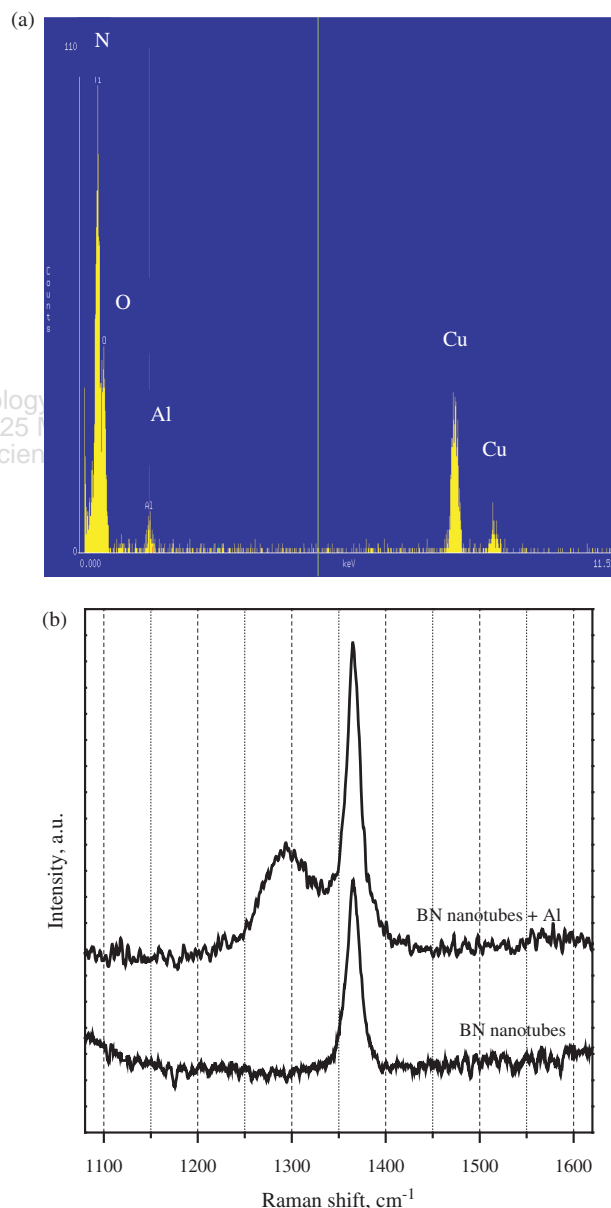

Fig. 3. Structure of BN nanotubes after Al ions implantation at 10–20 kV and 10 mA.

Fig. 4. (a) EDX spectra of Al-implanted BN nanotubes; (b) Raman spectra of BN nanotubes before (bottom) and after (top) Al ion implantation.

confirming that the ion modification influenced only the outer shells.

In order to reveal the composite structure in more details, EDX and Raman measurements were performed. The EDX spectra shown in Figure 4(b) confirmed the presence of Al atoms in the prepared nanohybrids. Besides the peak corresponding to aluminum, a marginal oxygen peak and a nitrogen shoulder were clearly seen in these spectra, evidencing a partial aluminum oxidation.

The Raman spectroscopy is known to be a powerful tool to detect the hexagonal BN materials and to analyze their crystallinity,[13–16] (although the resonant conditions could be reached only within UV region). The Raman spectra of the samples before and after ion modifications are shown in Figure 4(a). There are two characteristic features in the Raman spectra of crystalline hexagonal boron nitride materials: a low-frequency mode at ~ 52 cm^{-1}, corresponding to entire BN planes sliding vibrations; and a high-frequency mode at ~ 1366 cm^{-1}, corresponding to in-plane vibrations between B and N atoms.[13, 14] The low-frequency mode is usually difficult to observe due to the elastic scattering effects. The higher-frequency mode was observed in both samples. In the Al-modified sample a broad feature at ~ 1293 cm^{-1} was also detected. Similar downshifted peaks are typically seen in disordered phases of semiconductors, graphite, and diamond.[14, 15] The appearance of both features at 1366 cm^{-1} and 1293 cm^{-1} indicates that a partial amorphization of BNNT occurred as a result of Al ion implantation, and both phases (crystalline and amorphous) presented in the sample.

4. CONCLUSION

BNNT/Al nanocomposites were prepared by a high-energy Al ion implantation technique. The implantation parameters were chosen based on the previous investigations in order to obtain the structures with a uniform metal distribution. In high-energy ion-modified samples, the fibrous structures were observed by transmission electron microscopy. According to the energy-dispersive X-ray spectroscopy data these objects contained Al and marginal Al oxide in all cases. High-resolution TEM and Raman revealed that the BN crystalline phase had, at least partially, been preserved after the implantation in the interior

of these structures. The formation of BNNT/Al composite structures with different contents of metal and BNNT crystalline phases were observed. This novel nanomaterials are attractive for many technological applications, but their mechanical properties should first be studied in order to analyze a possible degradation of BNNT mechanical performance due to their partial amorphization and interaction with Al during the implantation procedure.

References and Notes

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