Nuclear Inst. and Methods in Physics Research, B 413 (2017) 31–36

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

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

Superhydrophobic to hydrophilic transition of multi-walled carbon nanotubes induced by Na^+ ion irradiation

Pritam Das[a], Satyanarayan Dhal[a], Susanta Ghosh[a], Sriparna Chatterjee[b], Chandra S. Rout[a], Niranjan Ramgir[c], Shyamal Chatterjee[a,*]

[a] School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Jatni, Khordha, 752050, India
[b] CSIR-Institute of Minerals and Materials Technology, Acharya Vihar, Bhubaneswar 751013, India
[c] Technical Physics Division, Bhabha Atomic Research Centre, Mumbai, India

ARTICLE INFO

Keywords:
Carbon nanotube
Ion beam irradiation
Welding
Wetting property

ABSTRACT

Multi-walled carbon nanotubes (MWCNT) having diameter in the range of 5–30 nm were coated on silicon wafer using spray coating technique. The coated film was irradiated with 5 keV Na^+ at a fluence of 1×10^{16} ions·cm^{-2}. A large-scale welding is observed in the post-irradiated nanotube assembly under scanning electron microscope. We have studied dynamic wetting properties of the nanotubes. While the pristine MWCNT shows superhydrophobic nature, the irradiated MWCNT turns into hydrophilic. Our simulation based on *iradina* and experimental evidences show defect formation in MWCNT due to ion irradiation. We have invoked mechanism based on defect mediated adsorption of water, which plays major role for transition from superhydrophobic to hydrophilic.

1. Introduction

Multi-walled carbon nanotubes are concentric tubes of graphene, having a large aspect ratio, light weight, strong, extremely good conductor of heat and electricity found to be a suitable material for research and industrial applications. Carbon nanotubes are being used as molecular quantum wires [1], metal-semiconductor contacts [2], gas adsorption [3], three dimensional CNT nanostructures for hydrogen storage [4]. In many applications knowledge of wetting property is crucial as there is need of controlling water content on the surface [5]. It is well known that both the chemical composition and the surface microstructures regulate the wettability of a surface. Contact angle (θ) between liquid droplet and surface is the measure of wettability. While θ below 90° is considered to be hydrophilic, the same above 90° is hydrophobic. Apart from surface energy, the roughness of nanostructured surface plays crucial role in controlling wetting behaviour. Sometimes the surface microstructures trap air, which can hold the water droplet and makes the surface superhydrophobic with contact angle in the range of 150°–180° [6]. Similarly, capillary effect of the microstructures can attract water strongly to the surface, which may lead to a hydrophilic or a superhydrophilic surface with contact angle approaching zero [6]. Carbon based coatings are usually known for their hydrophobic properties [7]. In fact deposition of carbon compounds from environment increases the water repelling nature of any surface. However, depending upon the surface morphology and crystal structure of carbonaceous material the nature of wettability varies. Earlier reports showed pristine CNT-covered surface mostly exhibit hydrophobic character [8]. Specially designed CNT array showed even superhydrophobic effects as reported by various authors [9–11]. Several methods have been explored in past to tune wetting behaviour of carbon nanotubes. For instance, UV irradiated carbon nanotube assembly showed a transition from superhydrophobic to superhydrophilic, which was attributed to defect formation induced by UV irradiation [12]. Only a small number of results on ion irradiation induced modification of wetting behaviour of MWCNT have been published so far. The present work aimed at modification of MWCNT with low energy ions and to explore the effect on its wetting behaviour. The MWCNTs have been coated on silicon substrate by spray coating technique, which shows superhydrophobic behaviour. The MWCNT coated substrate was irradiated with Na^+ ions. Here we demonstrate that low energy alkali ions can be used to switch a superhydrophobic MWCNT film to hydrophilic and these wetting properties are retained for long time. Such change in wetting behaviour is attributed to defect formation. The dynamic wetting behaviour has also been explored in this work.

* Corresponding author.
E-mail address: shyamal@iitbbs.ac.in (S. Chatterjee).

http://dx.doi.org/10.1016/j.nimb.2017.10.004
Received 3 September 2017; Received in revised form 18 September 2017; Accepted 2 October 2017
0168-583X/

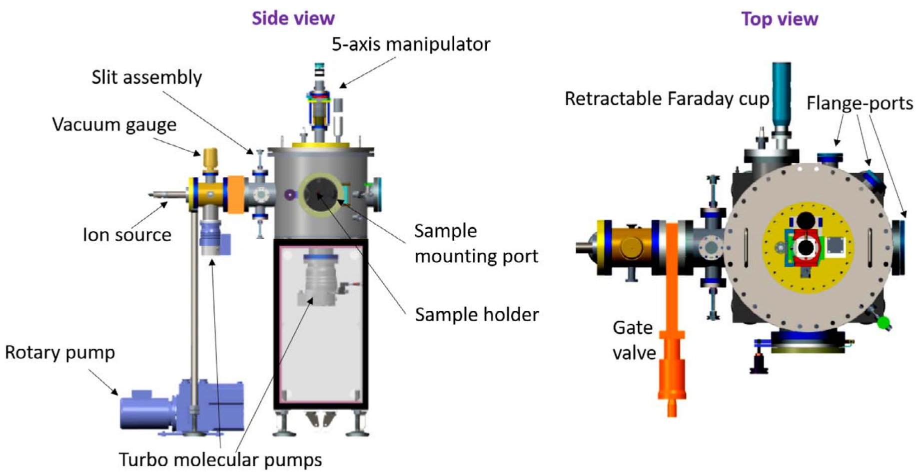

Fig. 1. Schematic of the ion-solid interaction setup.

2. Experimental

2.1. Preparation of MWCNT film on silicon substrate by spray-coating

MWCNT has been procured commercially (Reinste Nanoventure Pvt. Ltd, purity > 95%, number of walls: 3–5, outer diameter: 5–30 nm, inner diameter: 2–6 nm, length: 1–10 µm). Two milligrams of MWCNTs mixed in 5 ml ethanol (absolute; purity > 99.8% from Sigma-Aldrich) and the mixture was ultra-sonicated up to 1 h in an ultrasonic bath. This mixture was then spray coated on a preheated silicon substrate (high conductive, n-type, (100) oriented) at temperature of about 130 °C. The Si substrate was hydrophobic in nature and deposition of MWCNT layer on such hydrophobic surface was difficult as ethanol droplets were prone to form spherical droplets as soon as they touched the substrate. Use of high temperature (~ 130 °C) evaporates of ethanol was very fast, therefore, ethanol droplets had least time to roll off and an uniform coating of MWCNT was obtained. Distance between spray nozzle and substrate was ~ 20 mm. The coated substrates were finally air dried.

2.2. Na^+ ion irradiation on MWCNT film on silicon

The irradiation experiments have been performed in an indigenously developed ion-solid interaction setup available in IIT Bhubaneswar. A schematic diagram of the setup is shown in Fig. 1. The setup has two high vacuum chambers, for mounting the ion source and the sample, respectively. A vacuum of 10^{-7} Torr is achieved using turbo molecular pumps. The sample loading chamber has several additional ports for various uses, apart from sample loading window. Slit assemblies are used prior to the irradiation chamber to ensure uniform beam of desired size. A retractable Faraday cup is placed just before sample holder to assess the beam current and beam spot. A gate valve is used between the two chambers to isolate ion source from sample loading chamber. For the present experiment a uniform beam of Na^+ ions of diameter 1 cm bombarded the target at constant current of 1 µA. The Na^+ ions were delivered from ion source (Kimball Physics Inc.) mounted in the setup (see Fig. 1). The sample was mounted on a five-axis manipulator to optimize the beam spot to irradiate the entire sample uniformly. The X, Y, Z coordinates of the sample manipulator is in the range of ± 3 cm with precision of 1 mm, polar angle in the range of ± 90° and azimuthal angle for all 360°, respectively. The angular precision achieved is about 2°. Sample holder is electrically isolated and it has also provision to measure beam current for continuous monitoring purpose. Note that the beam was bombarded vertically to the sample surface.

2.3. Pristine and ion-irradiated sample characterization

The detailed structure and morphology were studied using Zeiss Olympus field emission scanning electron microscope (FESEM) and the crystal structure using a PanAlytical X'pert Pro powder X-ray diffractometer X-ray diffraction (XRD) at IIT Bhubaneswar and Raman scattering spectroscopy at IMMT Bhubaneswar. The surfaces of pristine and irradiated samples have been further examined with X-ray photoelectron spectroscopy (XPS) at IIT Kharagpur. The XPS system is PHI 5000 VersaProbeII (ULVAC–PHI, INC, Japan) with a microfocused (100 µm, 25 W, 15 KV) monochromatic Al-Kα source (E = 1486.6 eV), a hemispherical analyzer and a multichannel detector.

2.4. Wetting property measurement

Contact angle is the angle between the solid-liquid interface and the tangent of liquid-vapor interface at the contact point of solid-liquid-vapor. Sessile contact angle measurements of water droplet (deionized water (Millipore)) on both pristine and irradiated samples have been done at ambient temperature with drop volume of 5 µL using a contact angle measurement unit (Model No. OCA15EC from Dataphysics).

2.5. TRIM and iradina simulation

In order to explain the observed effects we have performed simulations based on TRIM [13] and *iradina* [14]. Both TRIM and *iradina* calculate the transport of energetic ions through solid matter by employing binary collision approximation in combination with Monte Carlo transport algorithm. In contrary to TRIM, *iradina* works on three-dimensional target geometries such as nanowire, nanotube etc within a rectangular grid of possibly up to several million cells with finite dimension. While input of both the programmes are energy and mass of the ions, fluence, target density, the output yields various results such as distribution of implanted ions, recoils, different types of defects, ion trajectories, recoil trajectories, final ion positions, distribution of deposited energy, sputtering yield etc.

3. Results and discussion

The surface microstructures of pristine as well as irradiated samples have been thoroughly investigated using scanning electron microscope. The scanning electron micrograph (Fig. 2(a)) reveals well separated nanotubes covering the substrate surface. The pristine nanotubes have diameter in the range of 5–30 nm with length in the range of 1–10 µm. However, drastic change in morphology is observed after ion irradiation. In Fig. 2(b) and (c), it is seen that Na^+ ion irradiation at an ion fluence of 1×10^{16} ions·cm^{-2} welds the nanotubes and form a nano-