

# Room-temperature growth of carbon nanofibers on plastic substrates

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## Abstract

A very simple method to synthesize densely distributed carbon nanofibers (CNFs) on flexible plastic substrates at room temperature with no catalyst is demonstrated. Carbon film was deposited onto polyimide, poly-ethylene-terephthalate (PET) films, Si plates and a Ni mesh, which were then sputtered with obliquely incident Ar<sup>+</sup> ions at 3 keV at room temperature. Linear-shaped CNFs oriented in the incidence direction of the ion beam grew on the sputtered substrates, as confirmed by scanning (SEM) and transmission electron microscopes (TEM). CNF growth on a PET substrate, which is a non-heat-tolerant plastic, has never been reported so far. CNFs thus grown were characterized as amorphous without a hollow structure. The diameter of CNFs was almost identical (20–30 nm) despite a large difference in CNF length (0.1–4 μm). In addition, the CNF-tipped cones were demonstrated to act successfully as a template to fabricate one dimensional (1-D) zinc oxide (ZnO) nanostructures on a PET substrate. Thus, it was believed that the ion-irradiation technique would open up a new approach to fabricate any kinds of 1-D nanomaterials on flexible substrates at room temperature.

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## 1. Introduction

Synthesis and application of low-dimensional carbon materials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), have become a topic of great interest in materials science and microelectronics technology since the discovery of CNTs by Iijima [1] in 1991. Arc discharge [1], laser ablation [2], and chemical vapor deposition (CVD) [3–5] have conventionally been used for their synthesis at temperatures usually higher than 500 °C. For a wider range of applications, however, synthesis at lower temperatures must be achieved. From this standpoint, plasma-enhanced CVD at and below 120 °C has been recently attempted [6,7].

Ion irradiation to solid surfaces sometimes entails the formation of various types of surface structures with nano-

to micro-meter dimensions. These typically appear as ripples, pyramids, conical protrusions and whiskers [8,9]. In our previous papers, it was demonstrated that oblique Ar<sup>+</sup> ion bombardment on a bulk carbon and carbon-coated metal and semiconductor surfaces induced the growth of conical protrusions and single CNFs grew on the tops even at room temperature [10,11]. Although the ion-induced growth of CNFs was limited to conductive substrates, myriad applications, e.g., flexible nano-electronics devices and memory media, would be possible if CNFs could be grown densely also on non-conductive plastic substrates at room temperature. Here we challenged the synthesis of densely distributed CNFs on plastic substrates at room temperature with no catalyst. In addition, in order to explore the possibility of the ion beam technique to the low-temperature fabrication of one dimensional (1-D) non-carbon nanomaterials, densely distributed zinc oxide (ZnO) nanoneedles were fabricated on plastic substrates using the CNF-tipped cones as a template.

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## 2. Experimental

Current microelectronics technology is based on Si technology, and plastics are widely used in memory media applications. Thus, samples employed were single crystalline Si(100) plates, commercially available PET and polyimide films. PET substrates, whose glass transition temperature and melting point are 67 and 258 °C, respectively, have never been tried for the CNT or CNF growth. For the structural analysis of CNFs by TEM, a Ni mesh (200 mesh) was also prepared. Prior to ion-induced CNF growth, diamond-like carbon (DLC; 1.5 μm in thickness) or amorphous carbon (500 nm in thickness) films were deposited onto them by hollow cathode deposition and sputter-deposition methods, respectively. These samples were further coated with porous carbon films.

The carbon-coated samples were then irradiated with 3 keV Ar<sup>+</sup> ions (JEOL; MIED) focused into a microbeam 380 μm in diameter in an ultra-high vacuum chamber (JEOL; JAMP-10 S) [10,12]. The incidence angle of the ion beam was 55° from the normal to the surface. Oblique-ion-bombardment is known to be more suitable for ion-induced CNF growth than sputtering at normal incidence [10,11]. In every experiment, sputtering was done at

room temperature. The chamber was pumped down to  $\sim 2 \times 10^{-7}$  Pa, and the pressure was kept at  $10^{-6}$  Pa region during sputtering, due to the differential pumping of the ion gun.

After sputtering, the topography of the sample surfaces and the crystallinity of CNFs thus prepared were carefully observed by SEM (JEOL; JEM-5600) and TEM (JEOL; JEM-3010), respectively. For TEM, the CNF-covered Ni mesh was directly mounted on a sample holder without any post-treatment.

## 3. Results and discussion

Fig. 1(a) shows an SEM image of the surface of a DLC-coated Si(C/Si) after sputtering, disclosing that densely distributed conical structure was formed on the sputtered surface and that single CNFs grew on almost all of the cone tops. No more than one CNF grew on the cone tops. In addition, no CNF formed without cone bases. The CNFs were linear in shape. It should be noted that the CNFs were almost uniform in diameter ( $\sim 20$ – $30$  nm) independent of the length (0.2–4 μm). As seen in Fig. 1(a), conical bases and CNFs were pointed in the ion-beam direction. A careful inspection of Fig. 1(a) revealed that

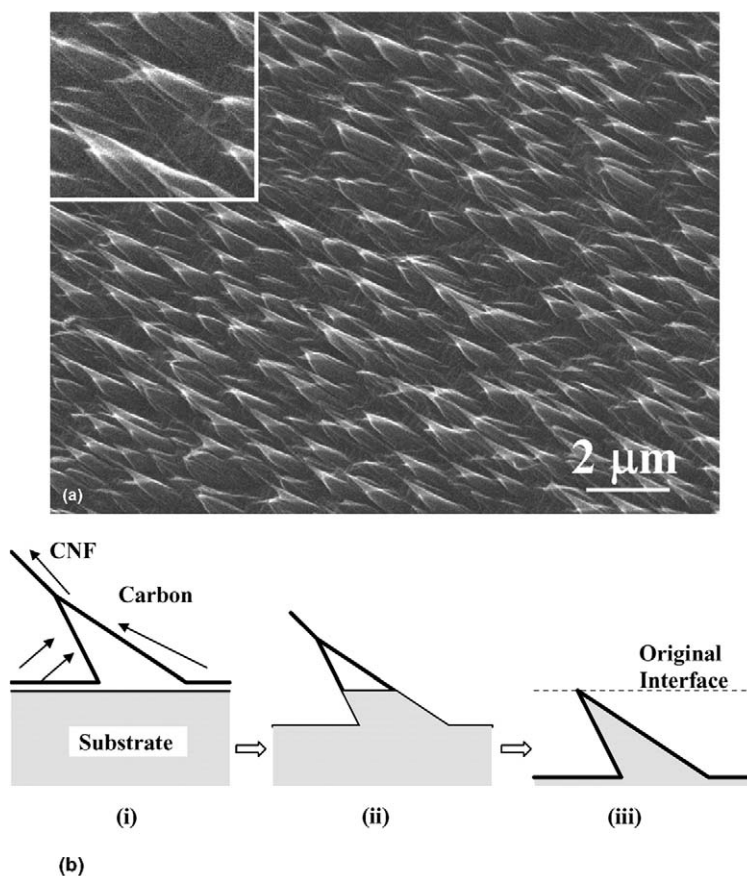


Fig. 1. (a) Side-view SEM image of the surface of a C/Si plate after ion bombardment. Inset: Enlarged SEM image showing CNFs grown on conical tops. (b) Schematic representation of a proposed formation mechanism of ion-induced CNFs and nanocones: (i) CNF formation, (ii) dual structural cone with CNF on top and (iii) nanocone formation.

the tip region of cones was more transparent in SEM contrast compared with the base region, suggesting the structural duality (see also Fig. 1(b)(ii)). (As will be confirmed later, the tip region of conical protrusions was composed of carbon.)

The formation mechanism of the ion-induced CNFs is thought to be as follows (Fig. 1(b)(i)): (i) Formation of conical carbon protrusions, (ii) redeposition of carbon atoms sputter ejected from the surface onto the side-wall of conical protrusions and (iii) surface diffusion of the redeposited carbon atoms toward the tops during sputtering, thus forming the CNFs on the cone tops. (A further discussion will be given later.)

Fig. 2 shows the morphological structure of a sputtered amorphous-carbon-coated polyimide (C/polyimide) film surface. Similar to the C/Si case, the sputtered surface was covered with densely distributed cones and single CNFs grew on the respective cone tops. The shape of CNF-tipped cones was almost identical with that grown on bulk carbon [10] and C/Si surfaces, and the structural duality was also recognizable. From Fig. 2, the numerical density of CNF-tipped-cones on the C/polyimide was estimated to be  $\sim 10^6/\text{mm}^2$ , which was comparable to that on the C/Si surface. CNFs thus grown on the C/polyimide ranged from 0.1 to 2  $\mu\text{m}$  in length independent of the size of cones, while they were almost uniform in diameter (20 nm). It should be noted that CNFs grew on amorphous carbon films as well as on DLC films. A further attempt of the CNF growth on non-heat-tolerant substrates was made using amorphous-carbon-coated PET (C/PET) films. The formation of CNF-tipped-cones on C/PET was confirmed similar to the cases of C/Si and C/polyimide. The present ion-induced method could be used even for temperature sensitive substrates such as PETs, thereby suggesting that it is a very low or close to room temperature process. From these facts, it was concluded that carbon pre-coating was quite effective to yield the ion-induced CNF-tipped-cones on any solid surfaces including plastics.

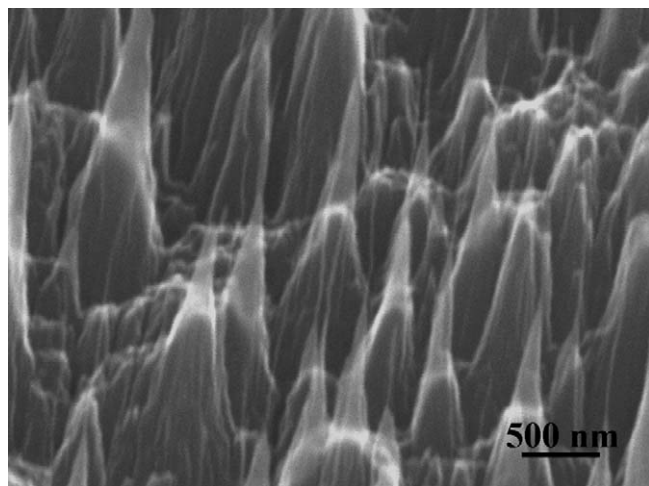


Fig. 2. SEM image of CNFs grown on a C/polyimide substrate after sputtering, viewed at  $30^\circ$ .

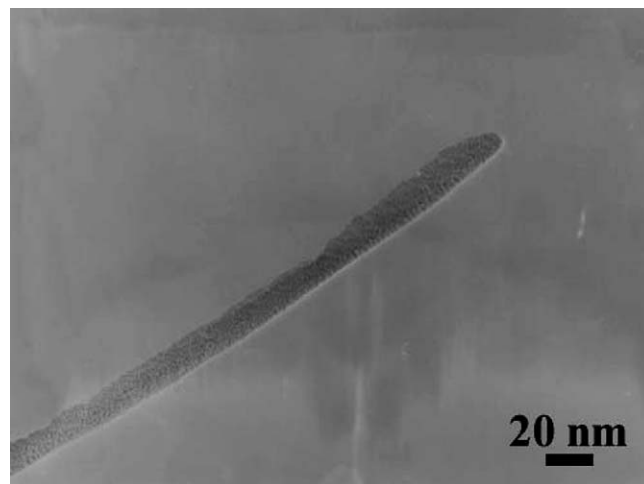


Fig. 3. (a) Typical TEM image of the tip region of a linear-shaped CNF grown on the C/Ni mesh. (b) Electron diffraction pattern taken at the CNF tip.

Fig. 3 shows a TEM image of the tip region of a typical CNF grown on a DLC-coated Ni (C/Ni) surface. No hollow structure was recognized in the CNF, identifying it as different from a CNT. The CNF was almost uniform in diameter,  $\sim 20$  nm, along the growth direction and virtually independent of substrate materials. The CNF had a round tip with the radial curvature of  $\sim 10$  nm. Fig. 3(b) shows an electron diffraction pattern taken at the CNF tip, disclosing broad concentric Debye rings. This suggests that the CNF is amorphous. No electron diffraction spot corresponding to Ni was detected for either the tip regions of cones or CNFs, suggesting that CNFs grew on carbon cone tips.

Ion-induced growth of fine fibrous protrusions has been observed for several material systems, such as Mo-seed/Cu-target and Si-seed/Au-target, after sputtering of target materials (Cu and Au in these examples) at elevated temperatures with a simultaneous supply of so-called “seed” materials (Mo and Si) that differ from the constituent materials of a sputtered target surface [13,14]. In these cases, seed atoms thermally diffuse toward the growth sites during sputtering, thus forming fibers. In other words, sample heating is a necessary precondition for fiber growth. In contrast, CNFs grew even at room temperature without seeding. It is still unclear, unfortunately, why only carbon displays a different nature from other materials. In their

studies of fine whisker growth on bulk graphite surfaces induced by a normal-incident ion-beam sputtering, Van Vechten et al. demonstrated carbon atoms readily migrate during sputtering as far as  $\sim 20 \mu\text{m}$  on the surface [15]. It is very surprising that such a surface diffusion of carbon atoms took place on carbon films even at room temperature, as shown in the present study.

As described above, the surface diffusion of carbon atoms is thought to be responsible for the CNF growth [10]. If it is the case, after the coated carbon film was sputtered away, the CNF growth should cease, because no carbon supply (no redeposition) occurs during sputtering. Thus, CNF should decrease in length, and finally disappear from the cone tops. In other words, CNF-tipped cones acts as a template to fabricate conical structure of any substrate materials (Fig. 1(b)).

In order to confirm this, we challenged the fabrication of ZnO nanocones on plastic substrates. Taking the advantage of the room-temperature process of this sputtering method, PET was employed as a substrate. ZnO thin films,  $1.1 \mu\text{m}$  in thickness, were first deposited on the PET foils, which is referred to as ZnO/PET, using a filtered cathodic vacuum arc (FCVA) technique [16]. After the deposition of amorphous carbon film (150 nm in thickness) and porous carbon onto the ZnO/PET sample,  $\text{Ar}^+$ -ion sputtering was carried out. Fig. 4 shows a SEM image of the sputtered surface, revealing that the densely distributed aligned ZnO nanocones formed. As we expected, several nanocones still possess CNFs on the tops (see arrows in Fig. 4). The nanocone size was estimated to be 190 nm in base diameter and 470 nm in height. Their numerical density was reached to be  $\sim 10^6/\text{mm}^2$ .

For the further characterization, sputter-induced ZnO nanocones were also analyzed by TEM. (Since the carbon/ZnO/PET sample could not be mounted on the TEM sample holder, carbon/ZnO/ $\text{SiO}_2$ /Si sample was alternatively employed for the TEM analysis.) Electron diffraction

and high-resolution TEM observations revealed that the nanocones were in fact indexed to be wurtzite structure of ZnO, and thus they maintained the crystalline structure of the ZnO thin film [17]. It should be also noted that only very sparsely distributed ZnO nanocones were formed after sputtering without any carbon pre-coating. This fact implied that CNF-tipped cones obviously acted as templates for the formation of densely distributed ZnO nanocones.

Since the 1-D ZnO nanostructures have conventionally been synthesized by metal vapor deposition [18] and thermal evaporation and condensation [19] at growth temperatures usually higher than  $500^\circ\text{C}$ , ZnO nanostructure array on a PET surface has never been reported so far. Thus, it was believed that the ion-irradiation technique would open up a new approach to fabricate nanostructure array on any solid substrate at room temperature.

#### 4. Conclusion

The ion-induced CNFs were successfully grown on any solid surfaces including non-heat-tolerant plastics at room temperature with no catalyst. CNFs thus grown were characterized as amorphous without a hollow structure, and were almost uniform in diameter, 20–30 nm, irrespective of the length, 0.1–4  $\mu\text{m}$ . Their numerical density reached the order of  $10^6/\text{mm}^2$ . CNF-tipped cones were also successfully used as a template for the low-temperature fabrication of densely distributed ZnO nanocones on a PET substrate. Thus, it was believed that the ion-irradiation technique would be promising as a new approach to fabricate 1-D nanomaterials on flexible substrate at room temperature.

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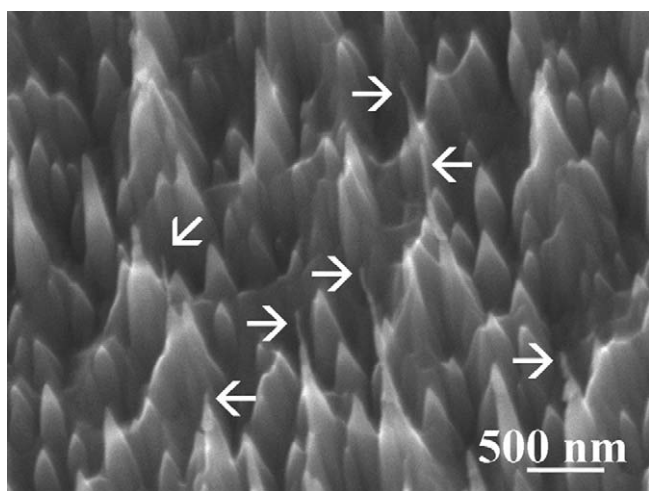


Fig. 4. SEM image of ZnO nanoneedles fabricated on a PET substrate, viewed at  $30^\circ$ . Arrows represent CNFs still that remained on the tops of nanocones.

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