Thin Solid Films 521 (2012) 102–106

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Highly efficient carbon nanotube growth on plasma pretreated stainless steel substrates

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ARTICLE INFO

Available online 15 February 2012

Keywords:
Carbon nanotube
Stainless steel
Surface pretreatment
Growth efficiency

ABSTRACT

We present here the direct growth of carbon nanotubes (CNT) on austenitic stainless steel (SUS316L) sheets containing catalytic elements that enable repeated growth without extra deposition of buffer and catalytic layers. We compared the effects of substrate pretreatment methods consisting of a combination of air-annealing and Ar-plasma treatment. The air-annealing and plasma-treatments were performed using a thermal furnace and cylindrical plasma chamber to induce morphological changes in the substrate surface. The roughness of the substrates was found to be considerably altered by annealing temperature, plasma pretreatment temperature, and growth temperature. The highest CNT height of 23.5 μm was obtained using SUS316L samples that were plasma-treated and air-annealed at 725 °C. Finally, the CNT growth efficiency was found to be enhanced considerably by the substrate pretreatments.

1. Introduction

Carbon nanotubes (CNT) have recently attracted considerable attention because since they have the potential for use in various fields owing to their outstanding physical, electrical, and chemical properties [1]. In some applications of CNTs, such as device interconnections, heat dissipation systems, electron emission devices, and charge collectors in energy storage or conversion devices, high conductivity at the CNT-growth substrate interface becomes a crucial factor, because the interface is the main barrier to electron and heat flow [2–6].

Among the available growth methodologies, chemical vapor deposition (CVD) has commonly been used to grow CNTs with an oxidative buffer layer, which facilitates efficient growth by preventing alloying between catalytic metals and substrates [7]. However, the CNT thickness should be minimized from the viewpoint of directional conductivity from the CNTs to the substrates used as charge collectors in the aforementioned applications. Thus, direct CNT growth on metal substrates is a very important, because it will enable expansion of their application areas. Additionally, it is still necessary to enhance the quantity of produced CNTs, because the amount generated using previously described methods was not satisfactory [8–10].

Here, we present the direct CNT growth on stainless steel (SUS316L) containing catalytic elements that enable repeated growth without extra deposition of buffer and catalytic layers. We focused on the effects of plasma pretreatments and air annealing on CNT growth behavior. Thus, we varied the order of plasma pretreatments and air annealing since these factors were expected to alter the surface morphology of the growth substrates, which is a crucial factor in the early stages of CNT growth. Significant enhancement in CNT quantity was achieved due to the response to plasma and subsequent annealing pretreatment of the substrates. The results presented here should contribute to expansion of CNT applications.

2. Experimental details

Commercial SUS316L sheets (0.1-mm thick) were used as the growth substrates because SUS316L contains catalytic elements for CNT growth, thus eliminating the need for depositing additional catalyst and oxide buffer layers. The chemical composition of the austenitic SUS316L was as follows: Cr (16–18 wt.%), Ni (10–12 wt.%), Mo (2–3 wt.%), Mn (<2 wt.%), Si (<1 wt.%), and others such as iron, nitrogen, phosphorous and sulfur. To investigate the effects of pretreatments on surface morphology, we varied the order of plasma pretreatments and air annealing. After mechanical polishing of the as-purchased SUS316L sheets, one substrate was prepared by Ar-plasma treatment (30 min) and subsequent air annealing (10 min) at 725 °C (PA pretreatment). Another substrate was prepared by air annealing followed by Ar-plasma treatment (AP pretreatment). The effects of the plasma power were also investigated by varying it from 7.5 to 14 W, which allows for a stable plasma state without arcing during pretreatment. The annealing temperature was also varied from 425 °C to 725 °C to investigate the possibility of low temperature growth in SUS substrates, which is important to ensure cost-effectiveness. To grow CNTs, the pretreated SUS substrates were inserted into a quartz tube (1-in diameter). The tube furnace was then heated to growth temperature under a reduction environment composed of a mixture of Ar (900 sccm) and H_2

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0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.02.043

(100 sccm), where it was held for 10 min to allow the furnace environment to stabilize. Next, CNT growth was induced by the introduction of acetylene (50 sccm), Ar (500 sccm), and H_2 (500 sccm). After CNT growth was allowed to occur for 30 min, the chamber was air-cooled to ambient temperature.

Atomic force microscopy (AFM, Park Systems X-70) in tapping mode operation, scanning electron microscopy (SEM, Coxem CX-100), and transmission electron microscopy (TEM, JEM2100F) were used for characterizing the surface structure and CNT morphologies. Top surface and cross-sectional SEM images of as-grown CNTs were taken. To directly confirm the CNT structure, we prepared a TEM sample by dropping a CNT solution onto a TEM grid and then allowing it to dry. Raman spectroscopy (Horiba Aramis), a powerful and convenient tool for estimating the structural completeness of CNTs by comparing the peak intensities of a structural-disorder-induced peak (D-band, ID) around 1350 cm^{-1} and tangential stretching vibration mode of graphite (G-band, IG) around 1590 cm^{-1}, was also employed [11].

3. Results and discussion

Fig. 1 shows the surface morphologies after the AP pretreatments. Fig. 1(a) and (b) depict samples subjected to air annealing at 425 °C and 725 °C for 10 min, respectively. After air annealing, subsequent Ar-plasma treatment was performed for 30 min at 10.5 W under 66.5 Pa. The 425 °C-annealed substrates were flatter than the 725 °C annealed samples.

To systematically investigate the effects of plasma power and annealing temperature on surface morphology, we varied the plasma power from 7.5 to 14 W during the plasma pretreatments at the fixed annealing temperatures [shown as red triangles and circles in Fig. 1(c)]. The annealing temperature was also varied from 425 °C to 725 °C with a fixed plasma power of 10.5 W [shown as black squares in Fig. 1(c)]. The Ra value, which is the arithmetic average of absolute values, was used for quantitative comparison of surface roughness. The Ra values from the samples annealed at 525 °C (red circles) were lower than those of the samples annealed at 625 °C (red triangles). The highest Ra value was recorded for the samples annealed at 625 °C and Ar-plasma-treated at 10.5 W. Overall, the annealing temperature had stronger effects on surface roughness; these effects were apparent at temperatures greater than 625 °C.

We also comparatively investigated the changes in surface morphology after the PA pretreatments (Fig. 2). Fig. 2(a) and (b) show the samples that were Ar-plasma-treated at 425 °C and 725 °C for 30 min at 10.5 W, respectively. After plasma treatment, air annealing was performed at 725 °C for 10 min. As shown in Fig. 2(a), the sample that was plasma treated at 425 °C appears very flat with wavy structures similar to those on a polished surface. Conversely, nanoparticle structures were formed after the 725 °C plasma treatment [Fig. 2(b)]. Fig. 2(c) summarizes the changes in Ra value at different plasma powers and

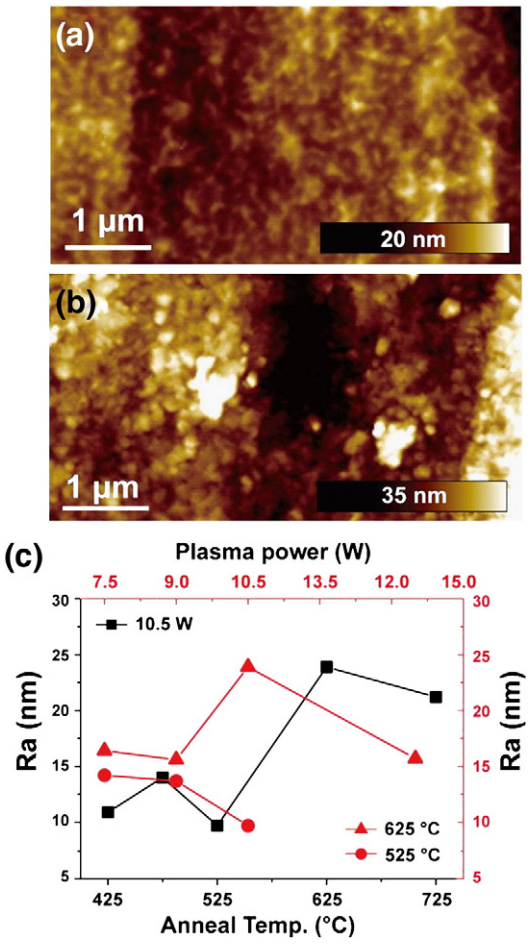

Fig. 1. AFM topographic images obtained after AP pretreatment. The air annealing was performed at (a) 425 °C and (b) 725 °C. (c) Variation of surface roughness with different applied plasma power (top and right axis) and annealing temperatures (bottom and left axis).

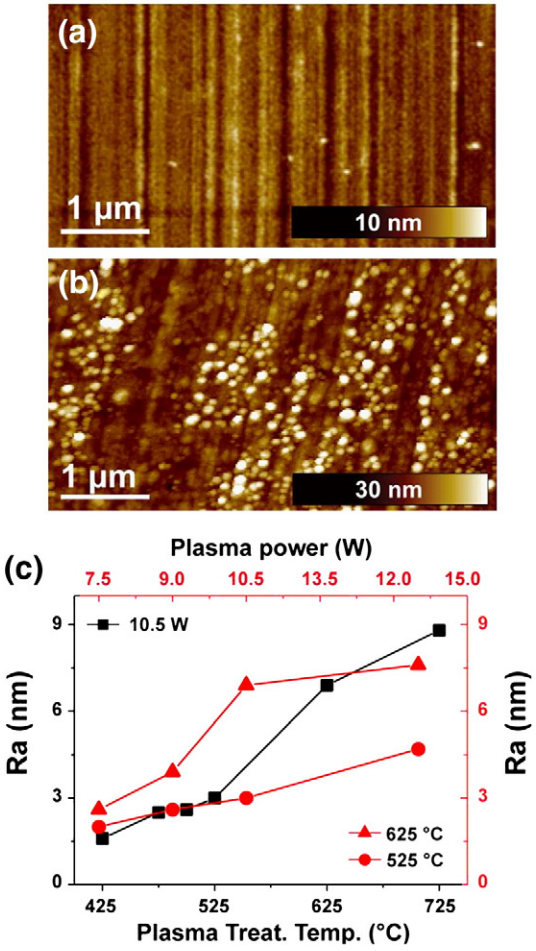

Fig. 2. AFM topographic images obtained after PA pretreatment. The Ar-plasma treatment was performed at (a) 425 °C and (b) 725 °C. (c) Variation of surface roughness with different applied plasma power (top and right axis) and plasma treatment temperatures (bottom and left axis).