

Low-temperature assembly of ordered carbon nanotip arrays in low-frequency, high-density inductively coupled plasmas

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Abstract

High-density inductively coupled plasma (ICP)-assisted self-assembly of the ordered arrays of various carbon nanostructures (NS) for the electron field emission applications is reported. Carbon-based nano-particles, nanotips, and pyramid-like structures, with the controllable shape, ordering, and areal density are grown under remarkably low process temperatures (260–350 °C) and pressures (below 0.1 Torr), on the same Ni-based catalyst layers, in a DC bias-controlled floating temperature regime. A high degree of positional and directional ordering, elevated sp² content, and a well-structured graphitic morphology are achieved without the use of pre-patterned or externally heated substrates. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

One of the ultimate goals in the bottom-up approach to the self-assembly of nanostructured matter is to achieve a reasonable control and predictability in the size, architecture and ordering of the nanostructures (NSs), which are the building units for a wide variety of mesoscopic functionalities and devices. Several applications, such as electron field emitters (EFEs) [1], require excellent ordering of the NSs both in the growth plane and in the growth directions [2]. Positional control in most of the existing nanostructure fabrication techniques is achieved by using pre-patterned substrates and expensive nano-lithography processes. Thus, the apparent challenge is to develop a suitable technique for the growth of the ordered self-assembled nano-islands that promote bottom-up assembly of the functional NSs thereon without any pre-patterning routines. However, the efficiency of the specific envisaged application also depends on a number of other requirements, including shape, internal organization and chemical structure, phase and elemental

composition, electrical/optical parameters, suitable mechanical and adhesive properties, and several others. From the manufacturing point of view, the number of steps required for the nano-assembly and subsequent device integration is to be minimized.

Self-assembled carbon nanotips (CNTPs) grown by chemical vapor deposition (CVD) on metal catalyst layers are promising for EFE applications as efficient field enhancing structures with size-dependent electronic properties [3]. One of yet unresolved puzzles is to synthesize the ordered CNTP arrays under the process temperatures well below the metallic interconnect melting points to enable the efficient integration of the NSs into electronic/photonic devices. Most of the existing CVD techniques based on a thermal decomposition of hydrocarbon feedstock gases fall short to meet the above requirement.

On the other hand, several plasma-enhanced CVD (PECVD) methods have recently proved efficient in the low-temperature synthesis of various carbon-based NSs (CNSs) and the process temperatures as low as 400 °C have already been reported [1]. The required ordering of the CNSs in the growth direction can be achieved by DC or RF biasing the substrate [4,5]. However, most of the existing plasma-based methods require the external substrate heating to activate the catalyst layer and promote the CN growth.

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Here, we propose a new method for the management of self-assembled carbon nanostructure arrays without pre-patterning of the substrate in the high-density chemically active environment of low-frequency (~ 460 kHz) inductively coupled plasmas (ICPs) and demonstrate that different architectures of the individual NSs can be achieved in the low gas temperature range of $260\text{--}350^\circ$ on the same metal catalysts by varying the DC substrate bias. The technique proposed does not require any external substrate heating and the necessary activation of the Ni-based catalyst layer is achieved by a combination of the reactive etching and surface heating by a hot neutral gas in the reactor chamber. In this way, it appears possible to control the site density and spacing as well as to achieve excellent uniformity of the CNTPs and carbon pyramid-like structures (CPLSs) over the large areas. Likewise, the NSs also feature an elevated content of sp^2 -bonded carbon, which are the favorable factors for the development of the EFEs.

2. Experimental

The nanostructures were grown in a low-frequency ICP reactor described in detail elsewhere [6] on ~ 30 -nm-thick Ni/Fe/Mn catalyst layers pre-deposited on lightly doped Si(100) substrates in a ultra-high vacuum sputtering reactor. The substrates were placed on the top surface of a DC-biased substrate holder positioned in the area of the maximal electron/ion density in the plasma reactor [6]. Reactive gases Ar, H_2 , and CH_4 were introduced into the chamber sequentially. A 30-min wall/substrate conditioning in Ar was followed by a 20-min catalyst activation in the Ar+ H_2 mixture. Thereafter, a carbon source gas CH_4 was fed into the chamber for the entire duration of the 40-min PECVD process. The partial pressures in the Ar+ H_2 + CH_4 gas mixture were maintained at 60, 17, and 8 mTorr, respectively. The high-density ($n_{e,i} \sim 10^{12} \text{ cm}^{-3}$, where $n_{e,i}$ is the electron/ion density) plasma was sustained with RF power densities of $0.09\text{--}0.11 \text{ W/cm}^2$. In the floating (DC bias-controlled) temperature growth regime of interest here, the substrates were heated internally by the hot working gas and intense ion fluxes.

3. Results and discussion

Fig. 1 shows FE SEM micrographs of the NSs grown at different DC substrate bias V_s . The corresponding variation of the substrate temperature T_s is given in Fig. 2, where and below the same numbering as in Fig. 1 is used. At zero DC bias (Fig. 1(i)), only nanoparticles and nanoparticle agglomerates partially cover the surface and there are no other NSs visible. We have observed that there is a minimum negative DC bias (in the $50\text{--}60 \text{ V}$ range) that enables the growth (with the average growth rate of $2\text{--}5 \text{ nm/min}$) of small (typically $10\text{--}20 \text{ nm}$ in width and $80\text{--}100 \text{ nm}$ in height)

carbon nanotips (Fig. 1(ii)). The minimum T_s for the nanotip growth is approximately 270°C . With an increase of the bias to -100 V (and the substrate temperature to $T_s \sim 310^\circ \text{C}$), the nanotips grow in size (Fig. 1(iii)) and their areal density (the averaged number of individual nanostructures per linear micron) increases as shown in Fig. 2. When V_s increases further to -200 V , the CNTPs disappear giving rise to the pyramid-like structures (typically $100\text{--}150 \text{ nm}$ in width and $400\text{--}450 \text{ nm}$ in height) shown in Fig. 1(iv). The minimum T_s that enables the growth of the CPLSs (with the average growth rate of $10\text{--}13 \text{ nm/min}$) is estimated to be $\sim 320^\circ \text{C}$. We note that the CNTPs are still observable at the substrate biases $V_s \sim 150 \text{ V}$ and temperatures $T_s \sim 300^\circ \text{C}$. The self-assembly of the CPLSs becomes pronounced and peaks at $V_s = -300 \text{ V}$ (Fig. 1(v)), when the substrate temperatures rise to $\sim 350^\circ \text{C}$. Meanwhile, the CPLSs areal density diminishes with DC bias, with approximately 4 structures per $1 \mu\text{m}$ at $V_b = -400 \text{ V}$, as can be seen in Figs. 1(vi) and 2. It is remarkable that all the resulting NSs are aligned vertically and perpendicular to the substrate surface. Physically, the direction of the DC electrostatic field is an energetically most favorable orientation of one-dimensional CNSs [7].

Thus, Figs. 1 and 2 reveal an excellent ordering and uniformity of the CNTPs and CPLSs both in the growth direction and over the large areas. Furthermore, even a modest change in the substrate bias ($\delta V_s \sim 50\text{--}100 \text{ V}$), results in a structural transformation of the CNTP arrays into CPLSs. Previously, similar transformations were reported for different CNSs [8]. We emphasize that the process temperatures and gas pressures in our ICP reactor are noticeably lower than in many relevant plasma-based methods [1,4,5,7–9].

A detailed SEM analysis also reveals that the CNTP structures in Fig. 1(ii) and (iii) do not grow on the nanoparticles and nanoparticle agglomerates (the latter also grow in size with bias and form large islands of irregular shapes) and follow tiny growth islands on the thermally and plasma-chemically activated catalyst surface. On the other hand, no more nanoparticle agglomerates can be seen when larger CPLSs start to self-organize into ordered surface morphology elements (Fig. 1(iv)). A further comparison of the surface morphologies of the catalyst-coated samples removed from the reactor chamber immediately after the hydrogen etching stage and those at the initial growth stages reveals a remarkable correlation between the widths of the CNTPs and the nano-islands created as a result of the reactive chemical etching (RCE). Presumably, the preferential growth of the CNTPs on the nano-island edges [9] is not the case in our experiments. Taken a small size of the growth islands, low temperatures of the process, and relatively large thickness of the catalyst layer, we can speculate that the RCE rather than the plasma heating is a dominant surface activation mechanism here.

Raman spectra of the films (Fig. 3a) exhibit two well-resolved G (at 1580 cm^{-1}) and D (at 1350 cm^{-1}) peaks

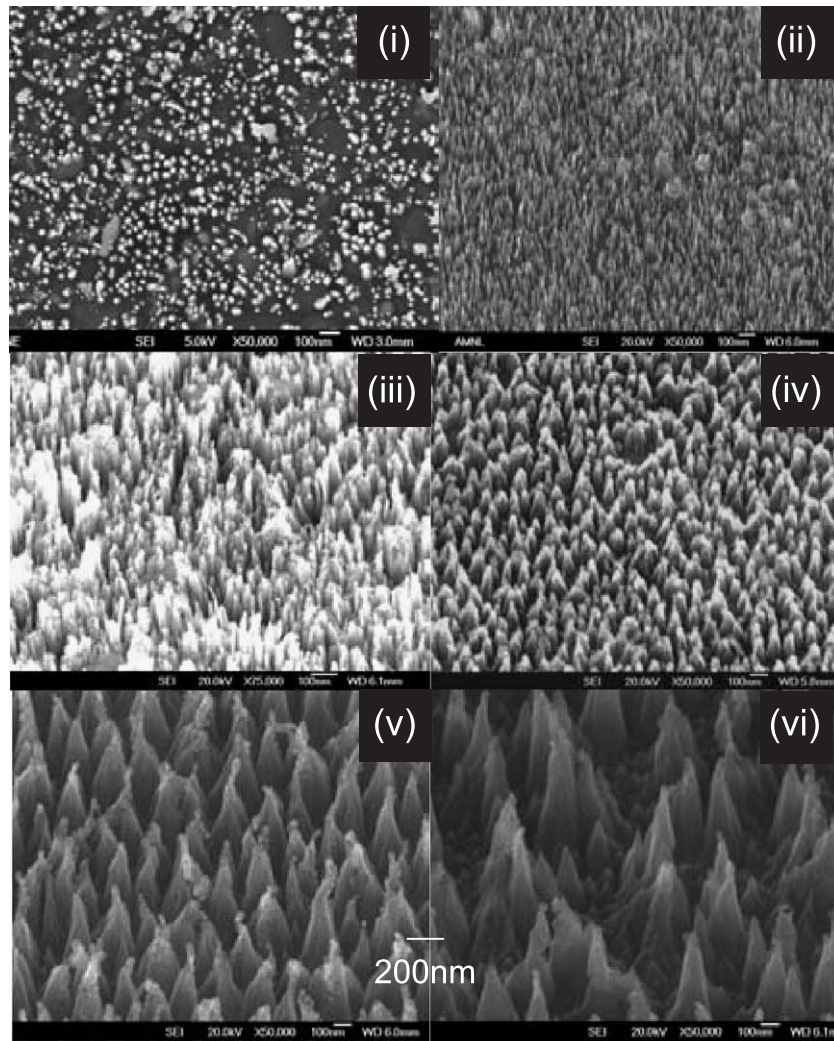


Fig. 1. FE SEM images of CNs grown at different DC biases. Micrographs (i)–(vi) correspond to $V_b = 0, -60, -100, -200, -300$, and -400 V, respectively.

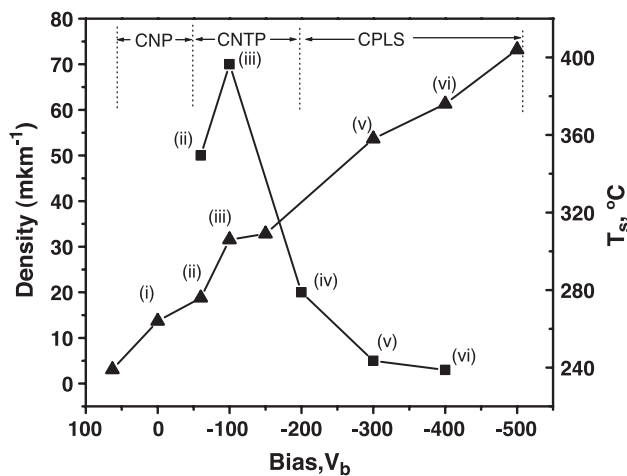


Fig. 2. Substrate temperature (triangles) and nanostructure areal density (squares) versus V_b for the same conditions [(i)–(vi)] as in Fig. 1.

suggesting the formation of a well-structured graphite-like morphology. A notable photoluminescence background indicates the presence of the disordered nanotip structures and large amounts of amorphous carbon (a-C) [9]. With an increase of DC bias, the ratio of the magnitudes of D and G peaks I_D/I_G grows, indicating a pronounced increase in the amount of unorganized graphite nanocrystals in the samples, as well as an increase in the number of nano-sized sp^2 clusters, which play an important role in the field emission from nanostructured carbons [10]. From Fig. 3a, one can note that the D peak is quite high and is comparable to the G peak, which indicates on the presence of microscopic defects in the structure.

It is also remarkable that the structures grown at $V_s > 200$ V are not only morphologically, but also structurally, different from those grown at lower DC bias. As can be seen in Fig. 3b, at $V_s > 200$ V, the XRD peaks (006) and (104) are split and a new peak at $2\theta = 29^{\circ}$ appears. Thus, the preferred

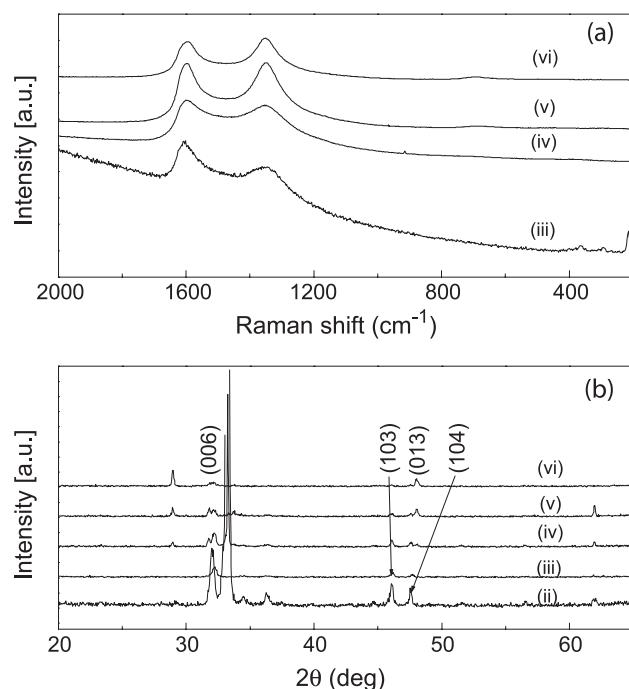


Fig. 3. Raman (a) and XRD (b) spectra of the films grown at the same conditions [(i)–(vi)] as in Fig. 1. In case (iii), the amplitude is multiplied by a factor of 10.

orientations of the crystal growth change when the formation of the CPLSSs is triggered. This can serve as a qualitative indicator of the enhanced growth of the pyramid-like structures.

It is quite likely that the films grown in our experiments contain at least two (crystalline and amorphous) carbon phases and can be termed polymorphous in a manner similar to nanostructured silicon-based films [11]. We also note that the resulting structures are strongly affected by the competition of the reactive chemical etching of the growth surface by hydrogen and PECVD of a new carbon material from the gas phase. In the low-temperature ($<350\text{ }^{\circ}\text{C}$) regime of interest here, a chemisorption of CH_3 radicals to hydrogen-terminated carbon surfaces is one of the most probable mechanisms of the carbon film growth [12]. In this case the CH_3 radicals stick to the surface as a result of a bias-controlled activation of the hydrogen-terminated carbon bonds by the impinging ions [12]. Hence, the activation of the nanostructured surfaces of our interest here can be controlled by the substrate bias voltage.

Apparently, the value of DC bias does affect the relative efficiencies of the competing RCE and PECVD processes. Generally, when the anisotropic etching prevails (at $50\text{ V} < V_b < 150\text{ V}$), the growth of high aspect ratio CNTPs is favored. At higher ($V_b > 200\text{ V}$) bias and substrate temperature, the RCE cannot keep the pace with the elevated amount of carbon material deposited onto the growing surface and extruded through the metal catalyst, so that the pronounced lateral growth evolves giving rise to the pyramidal structures (Fig. 1(i)–(vi)).

On the other hand, there is a minimum DC bias required for the nanostructures to start growing. Indeed, in the dissolution/precipitation growth mechanism, formation of NiC on the catalyst surface requires external supply of the energy ($\approx 9.8\text{ eV}$), which can be provided as a result of heavy particle collisions involving sufficiently accelerated (by the DC electric field) cations in the near-substrate sheath [1].

Remarkably low temperatures for the CNTPs growth can be attributed to the outstanding properties of the LF ICPs such as very high plasma densities, absence of high near-substrate self-biases common for many parallel-plate plasma reactors, and externally controllable ion fluxes onto the substrate [6]. In the plasma of interest here, the near-substrate sheath ($\sim 1\text{ mm}$) is smaller than the mean free path of CH_3 radicals, which is $\sim 1.76\text{ mm}$ at 85 mTorr . Thus, contrary to the case reported by Shiratori et al. [1], the LF ICP sheath is nearly collisionless. Our estimates also show that the bias-controlled cation fluxes onto the substrate are very strong and can exceed the diffusion fluxes of neutrals due to near-substrate density gradients.

The quite unexpected ability of the plasma–catalyst system to support the growth of the nanostructures at $T_s < 300\text{ }^{\circ}\text{C}$ can also be due to the excellent fragmentation of the Ni catalyst layer in this temperature range. Specifically, a lack of the fragmentation of Ni films on Si surfaces above $300\text{ }^{\circ}\text{C}$ was recently explained by the diffusion of Ni into the Si, leading to the formation of a silicide, NiSi_x [9]. It is yet another advantage of the technique proposed that no special barrier interlayers (such as SiO_2), adversely affecting the adhesion properties of the film, are required.

4. Conclusions

We have shown that a high-density chemically active environment of low-frequency ICPs is favorable for the low-temperature (below $350\text{ }^{\circ}\text{C}$) self-assembly of the ordered arrays of CNTPs and CPLSSs, wherein the ordering, areal density, and architecture are controlled by a competition of the RCE, PECVD, and growth island self-organization processes. Future work would include the study of the CNs growth dynamics and functionalization of the resulting nanostructures for the EFE and other electronic/photonics applications.

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