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On-Insulator Growth of Nanocarbons Ranging from 1D to 3D Morphology through Catalyst- and Seed-Free Plasma Chemical Vapor Deposition

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Particular interest has been given to 1D single-walled carbon nanotubes (SWNTs) and 2D single-layer graphene (*s*GPN) due to their unique physical and chemical properties among nanoscale carbon members (nanocarbons) with different dimensions [1]. Although metal catalysts have usually been used for their synthesis, their direct growth over insulators to bypass the transfer process would be highly desirable for extending their application fields [2]. However, this line of strategy has been handicapped by thermal chemical vapor deposition (TCVD) routes with extremely high reaction temperatures especially in the case of *s*GPN (*e*.g., 1000−1600 ℃). Here, plasma-enhanced chemical vapor deposition (PECVD) is for the first time applied to on-insulator catalyst- and seed-free direct growth of nanocarbons ranging from 1D to 3D, lowering the growth temperature down to 700 ℃.

Our experiments are performed using a PECVD system consisting of an RF(power: P_{RF})-discharge quartz tube and an electric furnace surrounding its center neighborhood. A quartz glass of typical insulator is adopted as a nanocarbon-growth substrate. Generated plasmas of electron density n_e and temperature T_e are provided to the substrate of temperature T_{sub} placed within the furnace site. Here an attention is given to the influx intensity and incident energy of ions on the substrate surface, which are measured as ion current I_i and difference between floating (φ_f) and space (φ_s) potentials, $\Delta\varphi = \varphi_f - \varphi_s$, yielding ion acceleration energy $U_i(= -e\Delta\varphi)$. Then, the plasmas are classified in three categories in accordance with I_i and U_i; (1) "very mild " ($P_{RF} < 20$ W: $n_e < 10^8$ cm^{-3}, $T_e < 0.3$ eV, $-\Delta\varphi < 1.0$ V) , (2) "mild" ($20 \lesssim P_{RF} < 40$ W: $10^8 \lesssim n_e < 10^9$ cm^{-3}, $0.3 \lesssim T_e < 1.0$ eV, $1.0 \lesssim -\Delta\varphi < 5.0$ V), and (3) "harsh" ($40\text{ W} \lesssim P_{RF}$: $10^9 \lesssim n_e < 10^{10}$ cm^{-3}, $1.0 \lesssim T_e < 4.0$ eV, $5.0 \lesssim -\Delta\varphi < 15$ V) plasmas (Fig. 1, I_i is normalized by 0.4 mA/cm^2). In an etching-effect experiment using graphene oxide (GO) ready beforehand, it is found that the perfect etching of GO occurs between T_{sub} =350 ℃ and 700 ℃. Then, the critical temperature 700 ℃ is designated as T_{sub} and the pressure ratio of H_2 is fixed to 12 % for 43 Pa of C_2H_5OH (carbon source) pressure. Raman scattering spectroscopy is mainly adopted on nanocarbon-characterization technique. In the case of TCVD (P_{RF}=0 W) only a very small peak of G(graphite)-band (∼1600 cm^{-1}) is observed in Raman spectra, indicating the growth of only some sort of carbonaceous matter (CM).

(1) Very mild plasma ($0 < I_i < 0.2$, $0 < U_i < 1.5$ eV) : Since apparent peaks of G-band and D(defect)-band (∼1330 cm^{-1}) appear, a material intermediate between amorphous carbon and GO is grown in this region.

(2) Mild plasma ($0.2 \lesssim I_i < 1.2$, $1.5 \lesssim U_i < 5.0$ eV) : Here the carbon-source supply and energy of ions impinging upon the quartz substrate are gradually increased to some extent. In addition to G- and D-band, clear Raman-spectrum peaks are often observed in the low-frequency range of 100-300 cm^{-1}, which is called as the radial breathing mode (RBM), verifying the growth of SWNTs. Concerning graphene remarkable peaks around 2660 cm^{-1} (2D band) in the high-frequency region are observed, the intensity of which is larger (*s*GPN) or smaller (a few-layers graphene: *f*GPN) than that of G band. Besides, the hybrid of 1D SWNT and 2D GPN, 3D nanocarbon, is confirmed to exist (*e*.g., inset of Fig. 1). The order of observation frequency can be summarized as follows: SWNTs ∼ *f*GPN > hybrid > *s*GPN.

(3) Harsh plasma ($1.2 \lesssim I_i < 5.0$, $5.0 \lesssim U_i < 15$ eV) : When P_{RF} exceeds 35 W, I_i and U_i jump about fivefold compared to those below it. Concomitantly, SWNTs, hybrid and *f*GPN disappear, and only sGPN grows in a uniformly-full coverage of fashion on the substrate surface instead. As for SWNTs, this phenomenon is understandable according to our previous study, where SWNTs were confirmed to suffer strong etching from ions in the U_i range of 10 eV [1]. The Raman study reveals that the grain size of *s*GPN (L_a) varies from the order of 100 nm to 10 nm when P_{RF} increases from 20 W over 40 W.

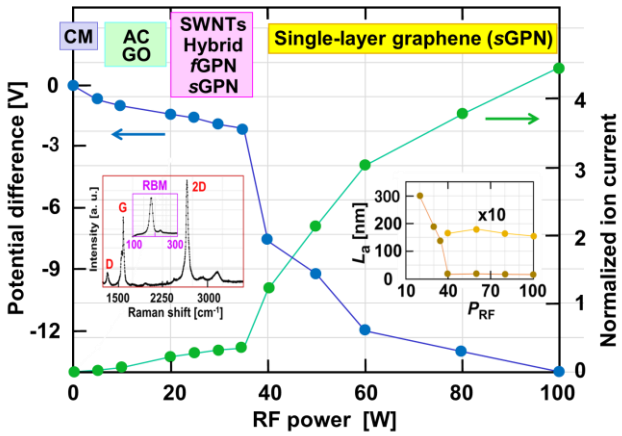

Fig. 1. Dependences of potential difference (Δφ) and normalized ion current (I_i) on RF power (P_{RF}). Insets show Raman-spectrum example of SWNT/*s*GPN hybrid and dependence of grain size L_a of *s*GPN on RF power.

References

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