Etching effect of carbon dioxide on carbon nanotube growth at high temperature

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[Introduction] Formed simultaneously with CNTs, amorphous carbon (a-C) adsorbs on the surface of catalysts or growth seeds and blocks the active sites. To remove such by-product, relied on oxidation reaction, kinds of etchants have been employed in the growth procedure. As part of the commoner used etchants, H_2O and CO_2 have been proved to perform some desired etching effects [1, 2]. In the reports we have presented before, when the growth temperature raised up to 1000℃, part of a-C might not be removed, especially when using ethylene as the carbon source [3]. This result reminded us the importance of etchant participated in growth system. In this project, we tried to figure out the etching ability of CO_2 in two-stage growth and made a comparison with H_2O. It has been found that, different with the etching capacity of H_2O performed at 1000℃, CO_2 prefers gentler etching effect with fewer CNTs damages even there got excess injection amount [4], which presented that the CO_2 could be a more efficient and stable etchant in CNTs' growth at high temperature.

[Experiment] Carbon nano-onion (CNO) was formed by heating nanodiamond at 1000℃ in Ar for 1 hour and works as the growth seeds. In the two-stage growth, the mixture of the growth gas is 4 sccm C_2H_4/Ar carried by 16 sccm H_2/Ar at 900℃ for cap formation and then turn to second stage growth, 1000℃, 30 min, while fraction of the carbon source was kept low (1 sccm C_2H_4/Ar carried by 19 sccm H_2/Ar). In one-stage growth at 1000℃, kept 2 sccm C_2H_4/Ar carried by 18 sccm H_2/Ar as the flow rate, the same amount of CO_2 has been injected and the injection time was adjusted from 0 min, 2 min 5 min, 7 min since the experiment starts. The growth result without CO_2 has been collected as the control. The quality and yield of the grown CNTs were characterized by Raman spectra using 633 nm excitation.

[Result and discussion] From Fig. 1, the Raman spectra shows the etching result comparison with various fraction of etchants at the second stage growth (1000℃, 30min). As Fig. 1a presents, the D band intensity didn't tend to show a distinct decrease even through there got excessive H_2O (250ppm and 300ppm) which has already prevented the a-C deposition on the blank sample surface and began to decrease the intensity of G band. This kind of excessive control of etching effect at high temperature limited the formation yield of high quality CNTs. On the other hand, CO_2, played a more stable etching effect which mainly focused on a-C oxidization without bringing too much defects at 1000℃, demonstrated by Fig. 1b. Combining with the further study about the influence of injection time at 1000℃ (Fig 2), the deposition of a-C should be very rapid and weaken the etching effect even if the CO_2 injection time delayed to 2 min so that the injection time should be start from the beginning. Also, the negative influence to CNTs crystallization could be ignored due to the D band intensity of the sample grown under CO_2 injection in the whole period and the formation of cap structure did not been prevented too much based on the G band observation frequency. In contrast to H_2O, it is supposed that CO_2 exhibits more suitable etching effect to enhance CNTs' growth at high temperature.

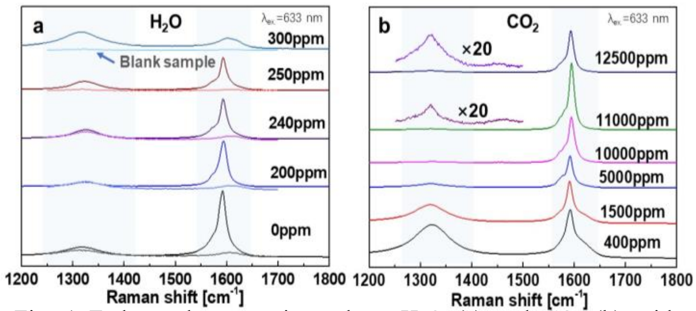

Fig. 1 Etch result comparison about H_2O (a) and CO_2 (b) with different injection amount at 1000 °C in two-stage growth system

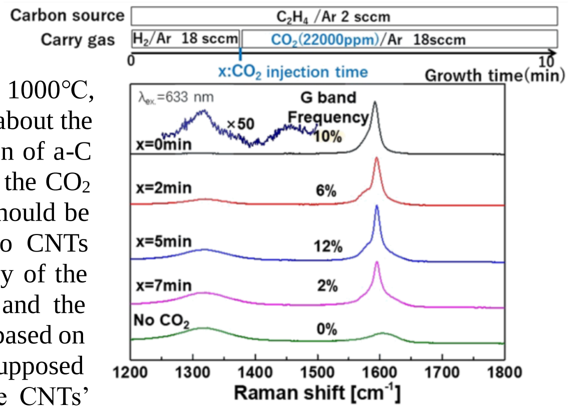

Fig. 2 1000℃, one-stage growth with various CO_2 injection time

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