論 文 の 内 容 の 要 旨

Abstract

論文題目　　CVD growth of super-small diameter single-walled carbon nanotubes

（超小径単層カーボンナノチューブのCVD合成）

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Single-walled carbon nanotubes (SWNTs), which have a unique one-dimensional structure of a rolled-up graphene sheet, are widely used for applications in many fields due to its outstanding optical, electronic, thermal and mechanical properties. Depending on the chirality of the SWNTs, SWNTs can be either metallic or semiconducting. One-dimensional structure of semiconducting SWNTs exhibits electronic quantum confinement effects, and the bandgap increases with the reducing diameter. The potential tenability diameter is expected to strengthen their applicability to solar cells with controllable band gap. Therefore, growth of smaller diameter SWNTs with higher band gap is a challenge both for application and in the fundamental point of view. In this work, super-small diameter SWNTs have been grown by extending the condition for chemical vapor deposition (CVD) from high temperature and high pressure to low temperature and low pressure. Also, the influences of the carbon feedstock and the catalyst on the growth rate and the properties of SWNTs have been also investigated.

Super-small diameter SWNTs are grown by alcohol-catalyst chemical vapor

deposition (ACCVD) method using USY-zeolite supported catalysts. In the conventional ACCVD process, usually, high-quality SWNTs can be grown around 800 $^{o}$C and 1.3 kPa. Through the investigations of the influence of temperature and pressure on the formation of SWNTs in this work, the relationship between the effect of temperature and that of pressure was clarified: SWNTs can grow at lower temperature when applied with lower pressure, which was also supported by the kinetic model on the formation of SWNTs. The temperature range for high-quality SWNTs could be extended down to 430 $^{o}$C in combination with very low partial pressure of ethanol down to 0.02 Pa. Extended-temperature range study opened a new operational window for efficient growth of small diameter SWNTs. During the experimental investigation with decreased temperature, super-small diameter SWNTs (0.8 nm > $d_t$ > 0.5 nm) were obtained around 500 $^{o}$C and 5 Pa. Previously, SWNTs with diameters smaller than (6,5) (~0.8 nm) have been known to be very difficult to grow except in a special zeolite pore or inside an outer nanotube. Super-small diameter SWNTs were rarely directly grown in reported works. By the low temperature growth with the conventional Fe-Co catalysts, we could extend the small diameter limit; ratio of smaller diameter tubes could be increased with low temperature CVD with optimum low pressure. Resonant Raman with five-color laser lines, absorption and Photoluminescence excitation spectroscopy (PL) are used to characterize and measure the abundance of small diameter nanotubes, and chirality of small diameter SWNTs were assigned as (6,4), (5,4), (8,0), (5,3), (6,1) etc..

On the other hand, in the expanded condition, SWNTs grown at high temperature and low pressure demonstrated relatively broad diameter distribution, which is similar to those grown by HiPCo method. It is a powerful way that small diameter SWNTs or broad diameter distribution SWNTs can be grown only by adjusting CVD experimental conditions without any specific catalysts or treatment. And obtained growth boundaries at too low temperature and too low pressure are promising for understanding the mechanism of SWNTs growth in Fe-Co ACCVD.

The influences of the feedstock (carbon source) and the catalyst on the formation of SWNTs were also observed. In the CVD synthesis of SWNTs, several processes limit growth rate and formation of SWNTs. In the gas phase, the feedstock compound experiences thermal decomposition before reaching the catalysts, gas- phase decomposition products are adsorbed and dissociate on the surface of catalyst, then the carbon atoms diffuse bulk or surface, and finally carbon atoms participate the growth of SWNTs. Different feedstock and catalysts behave differently during all these processes. Therefore, the effect of the feedstock and catalysts were also studied, especially for the low-temperature and low-pressure CVD synthesis of small diameter SWNTs.

Gas-phase thermal decomposition of ethanol, dimethyl ether (DME) and acetonitrile were simulated using the chemical kinetic model under various SWNT growth conditions. Time-profiles of species concentrations were demonstrated at various temperature and pressure. FT-IR spectroscopy was used to measure the concentrations of the products of DME and ethanol decomposition. FT-IR experimental results at various conditions were found to be in good agreement with the corresponding simulations. The simulation results indicated following: (i) Decomposition of ethanol affected the growth rate of SWNTs. (ii) However, cleaner SWNTs can be obtained at light decomposition condition of ethanol. (iii) For the condition of low-temperature and low-pressure CVD, the feedstock compound, ethanol, DME or acetonitrile directly arrives at the surface of catalysts almost without gas-phase decomposition.

Fe-Co catalyst was mainly used in this work, this effective catalyst assisted the exploration of CVD condition and super-small diameter SWNTs could be grown on it. In addition, Cu-Co and W-Co were also used to obtain specific SWNTs. By using Cu-Co catalysts, diameter distribution became narrower. The (6,5) SWNTs became predominant at 500 $^{o}$C. On the other hand, the (12,6) chirality became predominant when the fraction of W was increased in the catalyst of W-Co. Growth of super-small diameter SWNTs and the narrower chirality distribution suggest the promising future works for application and fundamental understanding of CVD growth of SWNTs.