Pinpoint Synthesis of Carbon Nanotubes using Focused Beams

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1. Introduction

Carbon nanotubes (CNTs) with their unique physical properties are expected to be new material for various applications, such as electronic circuits, electron and infrared emitters, and mechanical components [1]. Fabrication for the applications requires the position-control of CNTs on a substrate. Conventional researches have developed localizing catalyst technique in chemical vapor deposition (CVD) [2]. In this technique, catalyst islands are patterned in desired position on the substrate and then they are heated under carbon source gas in a furnace. On the patterned catalysts, CNTs are synthesized. However, it has some problems. The requirement of extra patterning complicates the fabrication process, and global heating causes thermal damage to every area. These suppress productivity and feasibility of the applications.

In this paper, we propose a novel position-control technique that localizes thermal energy by focused beams. CVD has three synthesis parameters: catalyst, thermal energy, and carbon source. We localize the thermal energy instead of the catalyst. In this technique, we provide thermal energy only in the selected position on the substrate and synthesize CNTs. The simple process and minimal heat of this technique offers easy production and high feasibility for the applications. Moreover, it can synthesize CNTs directly on semiconductor devices already patterned with aluminum. For the means of thermal localization we have studied two variant beams: electron and laser beam. Present paper shows experimental result of both methods.

2. CNT synthesis using focused electron beam

We used focused electron beam of scanning electron microscope (SEM) to localize thermal energy. SEM offers two functions: thermal localization with minute resolution and observation of the substrate. The maximum power of the electron beam is $3 \times 10^{-5}$ W, and the diameter is 1 nm. In addition to the thermal energy, CVD needs carbon source supply. To provide enough carbon supply into SEM and keep chamber pressure under the regulation for the observation, we developed Local CVD system (Fig.1), which introduces carbon source gas right in front of the catalysts with high density through a fine nozzle [3-4]. In case of insufficiency of the beam power, the system can assist rising temperature of the catalyst with substrate Joule heating.

Using Local CVD system, synthesis by electron beam was performed (Fig.2). We used Fe, Co particles supported with zeolite as the catalyst, and ethanol vapor as the carbon source [5]. In this condition, the catalyst needs the temperature of 600 to 900 °C for the synthesis. Experiment was performed as follows. The zeolite catalyst was placed on the substrate in the Local CVD system, and set in the SEM. After the evacuation of chamber, ethanol vapor with pressure of 130 Pa was supplied to the substrate. Then we began the observation. When a target zeolite was selected, electron beam irradiated to a point on the zeolite for 1 minute with 30 kV acceleration voltage and 1 µA specimen current (Fig.3). Irradiation was performed at various substrate temperatures up to 700 °C with the assisted heating.

As a result, CNTs were synthesized by the assisted heating, but the synthesis by electron beam could not be observed at any temperature. This result suggests the insufficiency of the beam power. According to Castaing, the temperature rise at the irradiated point is expressed as follows [6].

$$T = \frac{0.48EI}{\lambda d}$$  \hspace{1cm} (1)

Where T (K) is the temperature rise, E (V) the acceleration voltage, I (A) the specimen current, $\lambda$ (W/m·K) the thermal
conductivity of the target, and \( d \) (m) the diameter of the electron beam. In our case, when the electron beam carrying 1 nA at 30 kV with diameter of 1 nm irradiates the zeolite of which thermal conductivity is 0.55 W/m\( \cdot \)K, the temperature rise becomes 26000 K. It would be too high from our result. This inaccuracy results from the disregard of the penetration of electrons, which is not negligible in the calculation of nano-metered domain. By applying penetration theory to the calculation, we estimated accurate temperature rise. According to Kanaya et al., the maximum penetration range of electron is expressed as follows [7].

\[
R = \frac{2.76 \times 10^{-10} AE_0^{5/3}}{\rho Z^{8/5}} \left(1 + 0.978 \times 10^{-6} E_0^{5/3}\right) \left(1 + 1.957 \times 10^{-6} E_0^{4/3}\right)
\]  

(2)

Where \( R \) (m) is the penetration range, \( E_0 \) (eV) the incident energy, \( Z \) the atomic number, \( A \) (g) the atomic weight of the target, and \( \rho \) (kg/m\(^3\)) the density. The fraction of absorbed energy \( E_a \) (eV) as a function of depth from the surface \( x \) (m) is given by

\[
\frac{dE_a}{dy} = \frac{1}{\rho} \left(1 - \frac{y}{1-y} \right)^{2/5} \exp\left(-\frac{yw}{1-y}\right) \left(1 - \frac{3}{5} y + C \frac{6 \times 1.9}{5} \frac{y}{1-y} \exp\left(-\frac{1.9yw}{1-y}\right)\left(1 - \frac{1/2}{y} - (1-y)^{5/6}\right)\right)
\]

(3)

Where \( C \) is the experimental value ranging 0.6 to 0.8. In our case, with the zeolite of which atomic number is 10 and the atomic weight is 20, the maximum penetration range becomes 8.4 µm. Within 500 nm depths from the surface, the energy
absorption is 5.3% in initial energy, the power becomes $1.6 \times 10^{-6}$ W. In one dimensional heat conduction analysis with infinite cylinder model, the temperature rise at the surface is expressed as follows.

$$ T = -\frac{Q}{2\pi \lambda L} \ln\left(\frac{r}{r_1}\right) $$

(4)

Where $r$ (m) is the radial coordinate from the irradiation point, $Q$ (W) the heat transfer rate, $L$ (m) the characteristic length, and $r_1$ the radial coordinate at the boundary point. In our case, when the heat transfer rate is $1.6 \times 10^{-6}$ W, the characteristic length is 500 nm, and the radial coordinate at the boundary point is 1000 nm. The temperature rise at the center is 7.1 K (Fig.4). This result indicates that the beam has little effect for the temperature rise. This estimation suggests further improvements for the synthesis: the prevention of the electron penetration with reduction of acceleration voltage and use of high-atomic-number target, and the increase of the beam power with specimen current.

3. **CNT synthesis using focused laser beam**

For localization of thermal energy, we used continuous YAG laser beam with 1064 nm in wavelength. Laser can provide greater power than the electron beam. By contraries, the beam diameter becomes much larger because of its diffraction limit. The maximum power of the laser is 4.0 W. The beam diameter can be focused into 18 $\mu$m by optical lens. Same as the case of electron beam, the temperature rise of zeolite is determined by its absorption efficiency of laser beam. In one-dimensional thermal conduction analysis with infinite plate model, which assumes uniform intensity of the beam and sufficient heat transfer to the substrate. The temperature rise of zeolite is expressed as follows.

$$ T = \frac{4Q}{\lambda \pi d^2} \left( e^{-\alpha d} - \frac{1}{\alpha} + L \right) $$

(5)
Where $\alpha$ (m$^{-1}$) is the absorption coefficient of the target, and $d$ (m) the diameter of the laser beam. When the laser beam carrying 4.0 W with diameter of 18 $\mu$m irradiated to the zeolite of which characteristic length is 500 nm and absorption coefficient is $1\times10^6$ m$^{-1}$, the temperature rise becomes 14000 K. This estimation indicates that the absorption coefficient above $1.8\times10^5$ permits enough temperature rise for the synthesis.

The experiment was performed as follows (Fig.5). Fe, Co particles supported with zeolite was placed on a Si substrate, and set in a vacuum chamber. After evacuation, ethanol was supplied to the chamber at 2000 Pa. Then the laser beam irradiated to a spot on the substrate for 5 minute at the power of 350 mW with the diameter of 18 $\mu$m. After the irradiation, the substrate was analyzed with SEM and Raman spectrometry. Fig. 6 shows the SEM image of the irradiated spot. Laser beam printed circular trace in the center, in which bundles of CNTs were observed on a zeolite. The zeolite partially melted. Fig.7 shows the Raman spectrum of CNTs. G-band (about 1590 cm$^{-1}$, represents graphitic structure) and D-band (about 1350 cm$^{-1}$, represents defect in the graphitic structure) were observed. Both peaks were weak and fraction of G-band to D-band was smaller than usual. It indicates the low-amount and low-purity of CNTs.

The results proved synthesis of CNTs by localization of thermal energy. CNTs were synthesized in the center of the irradiated spot. It indicates that only the zeolite in the center got suitable temperature for the synthesis. However the melted zeolite and small fraction of G/D peak indicates that the temperature was a bit higher than the optimal temperature of 900 °C. The temperature distribution in the irradiated spot was attributed to Gaussian intensity profile of the beam. The temperature of zeolite became higher when it got near to the center. When we consider the temperature of the zeolite to be 1000 °C, the absorption coefficient of the zeolite is estimated to be $1.0\times10^7$ m$^{-1}$. For the control of synthesis area and quality of CNTs, further optimization of the laser power and beam diameter is needed.

4. Conclusion

In this paper, we presented a position-controlled synthesis for CNTs by localization of thermal energy using focused electron and laser beam. For the synthesis using electron beam, we used SEM with power of $3.0\times10^{-5}$ W and diameter of 1 nm. In the experiment, synthesis by electron beam could not be observed because of the insufficiency of beam power due to its penetration. Applying penetration theory, the temperature rise was estimated to be 7.1 K. Improvements that were prevention of the penetration and increase of specimen current were suggested. For the synthesis using laser beam, we used YAG laser with power of 350 mW and diameter of 18 $\mu$m. In the experiment, CNTs were successfully synthesized. It proved the synthesis by thermal localization. The synthesized area was smaller than the beam diameter due to Gaussian distribution of the beam intensity profile. Further optimization of the laser power and diameter are needed to control the synthesis area and quality of CNTs.

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