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# Dependence of catalytic nano dots prepared Si substrate in carbon-nano tubes growth

Shin-ichi Aoqui, Takahiko Uematsu* and Takamasa Sakai**

Sojo University, Ikeda 4-22-1, Kumamoto, 860-0082

Fax: +81-96-236-3000, e-mail: aoqui@cis.sojo-u.ac.jp

*ELIONIX INC, Motoyokoyama-cho 3-7-6, Hachioji-shi, Tokyo, 192-0063

Fax: +81-426-26-9081, e-mail: uematsu@elionix.co.jp

**Kumamoto Tech. & Industry Foundation, Tabaru 2081-10,

Mashiki-machi, Kamimashiki-gun, Kumamoto, 861-2202

Fax: +81-96286-3929, sakai@kmt-ti.or.jp

The gas occlusion alloy that a metal atom was used for an application to the fuel cell and so on. However the price of rare metals and a few amounts of gas occlusion to the unit weight causes a problem. A gas occlusion of carbon-based material attracts attention recently. Especially, as for the carbon nanotubes (CNTs), it began to be known that sensitivity for gaseous such as $NH_3$ and $NO_2$. Several processes such as arc discharge, chemical vapor deposition and pulsed laser ablation have been used to produce CNTs. However, it isn't easy to apply it a catalytic rare metal with low cost and high yield, which is necessary for the CNTs growth. In this study, a way that we applied a catalysis organ-metal solution to a Si substrate and then it was burned out was used. This method is very unique and low cost.

Key Words: carbon nano tubes, metal nano dots, organ metal solution, CVD

## 1. INTRODUCTION

Ever since the discovery of carbon nanotubes (CNTs), a lot of efforts have been given to utilizing their unique electric, structural and chemical properties. That is to say, CNTs have been focus of considerable attention because of many possible applications in nanostructure, super strong materials, low friction materials, semiconductor, electron emitting device, hydrogen storage, gas sensor and gas occlusion materials. [1-3] Especially, as for the CNTs it began to be known that sensitivity for gaseous such as $NH_3$ and $NO_2$, and also gaseous occlusion ability should be high. [4-6] If large quantities of gaseous can occlude CNTs, atmosphere release of the hazardous material such as Dioxin and NOx may be able to be controlled. [7] And also when an electric device is used for environmental application, many conditions must be satisfied such as low preparation cost, easy-spreading wide area, simple and safe preparation system and so on. Regarding to CNTs, several process methods such as arc discharge, chemical vapor deposition (CVD) and pulsed laser ablation (PLA) have been used to produce it. [8][9] However, as for which methods as well, it isn't easy to apply the catalyst metal, which is necessary for the CNTs growth. In this study, we did the experiments for the purpose as followings;

1. Form the metal(s) which becomes a catalyst for CNTs easily in the wide area preparation.
2. Investigate the characters of the metal dots.
3. Prepare CNTs growth on those metal dots.

In order to prepare large surface aria on small substrate, the way that we applied a catalysis organ-metal solution to a substrate and then it was burned out was used. [10] This method is very unique, especially it has almost never used as the catalyst for the nanotubes. Nano size dots of catalytic metal such as platinum (Pt), and Nickel (Ni), Ruthenium (Ru) on Silicon glass substrate preparation technique by burning of catalysis organ-metal solution had already been developed by pervious our work. In order to confirm the CNTs growth we used thermal CVD system

which is equipped high temperature electrical furnace. The temperature range of the furnace is up to 1600 °C. About carbon source we used to methane ($CH_4$) or ethylene ($C_2H_4$) gas. Also we carried out a effect of mixture of two catalytic organ-metal solutions and a selective growth of CNTs on mixture organ-metal solution those were Au/Pt and Au/Ni because Au has no catalytic effect. In growth of CNTs, catalytic metal might be small quantity. When CNTs is used to a gaseous sensor, it should be had to add an electrode to CNTs, but device preparation might be allowed in one path process, if Au metal which has no catalytic effect and good electrode material, and catalytic metal are mixed.

In this paper, we investigated intensively about CNTs growth on many kind of catalytic metal dots by using CVD system. Especially we concentrated to check the metal dot characteristics about the size, height occupation ratio of substrate. The CNTs were deposited in the temperature range from 600 to 1100 °C. The nano size metallic dot was characterized by a 3 dimensional electron probe surface roughness analyzer (3D-SEM), X-ray diffraction spectrometer (XRD), and scanning ion microscope (SIM), and deposited CNTs were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM).

## 2. EXPERIMENTS

On thermal CVD we used electric furnace which was work temperature range of up to 1600 °C. The substrate with organ-metal solution was burned out atmospheric pressure condition at 300,500, 700 and 900 °C in the furnace. After a reaction tube ($Al_2O_3$, $\phi$ = 50 mm) was exhausted by a vacuum pump to a base pressure of $1.0 \times 10^{-2}$ Torr. In order to prepare CNTs, n-type Si(100) wafer substrates, which the organ-metal solution which was called resinate ( Pt: A-1121N, Ni: 58-A, Au: 1118N, Ru: A-2575, all resinates were made by Engelhard Corporation) was spread by using spin coater, were positioned lower inside the tube. Fig. 1 shows general formula of organ-metal solution. [10] The substrates were heated from room temperature to 800 °C - 1600 °C. Substrate temperature (Ts) was measured by using a thermocouple. The gas pressure was varied from the base pressure to 100 Torr with 100sccm flow rate by feeding pure $CH_4$ gas or $C_2H_4$ gas , that was mixture a Ar gas.

$$(R-NH-)_l M(-O-\overset{\overset{O}{\|}}{C}-R)_n$$

M: Metal atom
R: Hydro carbon

Fig.1 General formula of organ-metal solution

## 3. RESULTS AND DISCUSSIONS

### 3.1 Metal dots characteristics

Though we discuss Pt dots to a typical example, a tendency is the same as to Au, Ni, Ru dots and those mixtures dots. The burning temperature dependence surface morphology of Pt catalytic metal dots on the Si substrate which should be used for the CNTs growth was examined by 3D-SEM, as shown in Fig. 2.

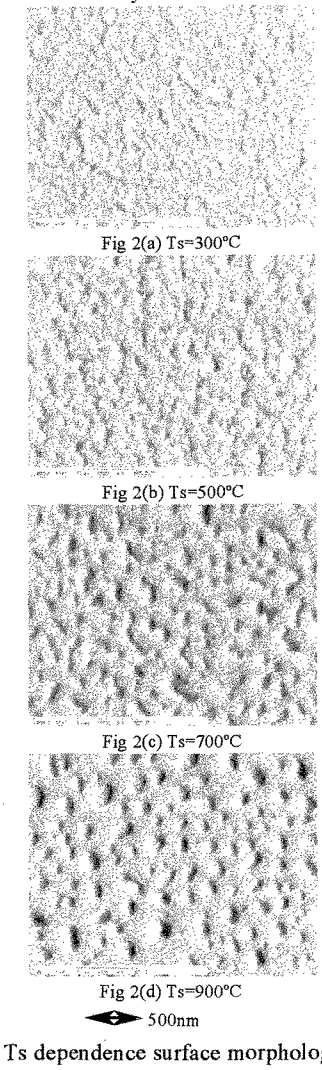



Fig.2 Ts dependence surface morphology of Pt

When the burning temperature was 300 °C, it was a very smooth morphology with a silver mirror

condition. When temperature rises up to 900 °C, Pt makes a dot type island-shape structure. Moreover dot can be classified in three kinds of diameter, such as about 30 nm, 60 nm and 120 nm. Fig. 3 shows full 3D image of Fig.2 (d). The height of the Pt dots increases caused by the rise in the burning temperature.

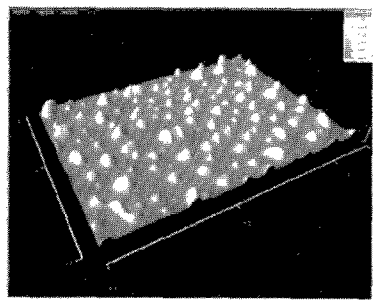


Fig.3 3D image of Fig.2 (d) Pt dots,Ts=900°C

The area ratio of the dots to the substrate area is shown in the Fig. 4. The 2-dimensional areas of the dots deceased caused by the burning temperature rise. Because Pt doesn't vaporize within900°C (Pt melting point: 1769 °C, boiling point: 3800 °C), the volume of the Pt metal doesn't decrease. Therefore, dots height should increase by a decrease in dots area ratio. However, the total metal volume, which calculated from the height measurement by 3D-SEM and dots area, decreased.

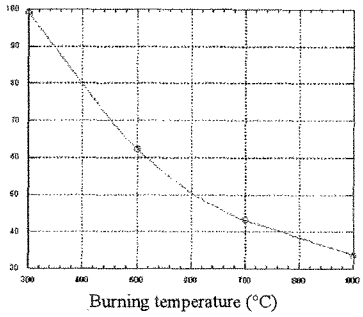



Fig. 4 Temperature dependence of the area ratio of the dots to the substrate area

The cross section of Si substrate was observed with a SIM to investigate the reason. The SIM system etches the substrate with a ion beam. Fig. 5 shows the image of the cross section of substrate with the dots. As for the Pt dots, it was confirmed that it was buried in $SiO_2$. About $SiO_2$ layer, generally it knows that it grows rapidly by burning a Si substrate in the atmospheric condition. Therefore, the volume of the observed dots decreased.

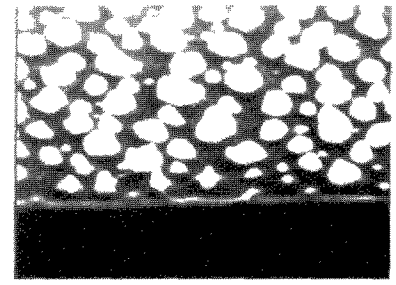


Fig. 5 SIM image of the substrate cross section

Now we consider that these dots have a different surface direction from the observation of XRD measurement, such as (111), (200) and (220) respectively. Fig. 6 show a temperature dependence of XRD spectrum pattern of Pt. (2q angle of (220) was not listed. It should be appear 65°. ) Crystallite sizes were calculated by Scherrer equation using FWHM of each peak. In Pt dot case, crystallite size of (111) peak is 26.7 nm, (200) is 42.7 nm and (220) is109 nm. These values show good agreement at diameters of a Pt dot. Though generally, between crystallite size and grain size don't have direct relationship, this is a surprising thing.

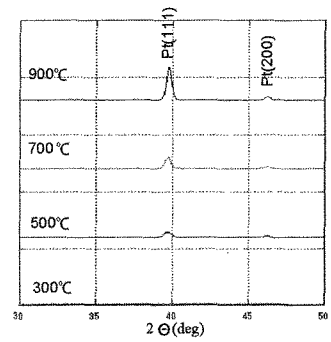
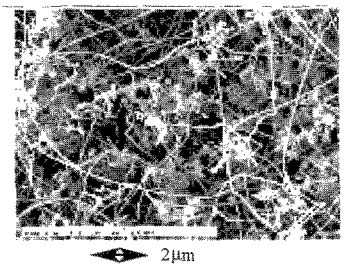



Fig. 6 Temperature dependence of XRD crystalline properties of Pt film on Si substrate

3.2 CNTs growth on catalytic metal dots

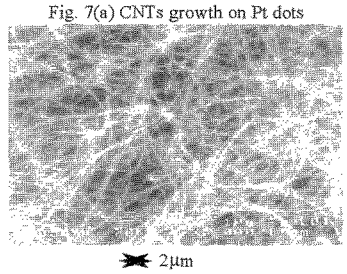
Fig. 7 show 3D-SEM images (it is not 3D images but normal SEM images) of the CNTs prepared by the CVD using Pt, Ni, mixture Au/Pt, mixture Au/Ni catalyst substrate at Ts = 1000 °C, $CH_4$ gas ambient. Reaction time was 30 min. Also we carried out the experiment of the selective growth of the CNTs. Because it doesn't have a effect of catalyst with Au, the substrate that the solution on which mixed a little (about 2 weight %) Ni or Pt to Au organ-metal solution was used for was burned out at 900 °C on 100 Torr Ar ambient condition. CNTs growth can be

confirmed. Typical tube diameters were 80 nm, 60 nm, 80 nm, 60nm respectively. Although CNTs grows very long and flexibly with a Ni catalyst, it seems to be hard to grow with a Pt catalyst. This is based on the difference in effect on the catalyst, but in case of Pt, improvement of flexible growth should be possible for that by control of reaction temperature and ambient gas kinds and flow rates.



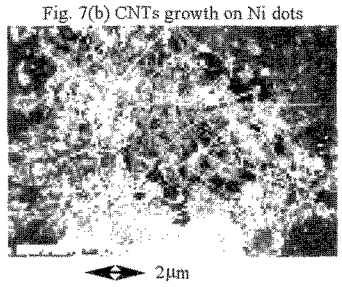
2μm

Fig. 7(a) CNTs growth on Pt dots



2μm

Fig. 7(b) CNTs growth on Ni dots



2μm

Fig. 7(c) CNTs growth on Au/Pt dots

Fig. 7 CNTs growth on various catalytic metal dots by thermal CVD using $CH_4$ gas ambient condition.

Also we carried out on CVD by using $C_2H_4$ gas ambient condition. flow rate and reaction temperature was same as $CH_4$ ambient condition but a reaction time was 5min, it was different from $CH_4$ CVD conditions. In this case we used Ni, Ru, and mixture Ni/Ru (1:1 ratio) metal dots. Fig. 8 shows the CNTs images of 3D-SEM. On Ni dots (Fig. 7(a)), tube diameter was about 3 times thick on the condition which $C_2H_4$ gas was used for comparison with $CH_4$. By using $C_2H_4$ gas, we could not confirm CNTs growth on Ru dots,and also as for the Ni/Ru mixture as well, it was not a normal tube, even if the process reaction time was shorter than $CH_4$ condition, it is shown Fig. 8(b).

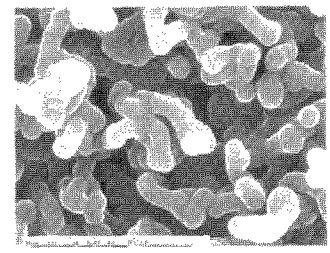


Fig. 8(a) CNTs growth on Ni dots

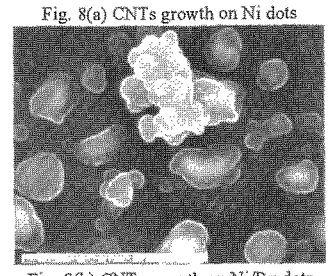


Fig. 8(b) CNTs growth on Ni/Ru dots

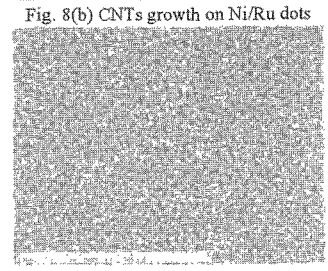


Fig. 8(c) CNTs growth on Ru dots

1μm

Fig. 8 CNTs growth on various catalytic metal dots by thermal CVD using $C_2H_4$ gas ambient condition.

## 4. CONCLUSIONS

In this study, CNTs were prepared using very new technique, which makes an organ-metal solution departure catalytic material. We confirmed many kind of organ solutions. This technique is very simple therefore it has a possibility of large-scale composition with lower cost. Also we confirmed selective growth of CNTs.

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