Pinpoint chemical vapor deposition of carbon nanowire for nanometer-scale electronic devices

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1 Introduction

This paper reports the method to generate a carbon wire of tens nanometers in diameter (carbon nanowire) in a desired (”pinpoint”) position for nanometer-scale electronic device. Recently, research which fabricates single-electron devices with carbon nanowire is widely done[1][2]. However, by the conventional methods, such carbon nanowire can not be generated in a desired position. So we developed pinpoint chemical vapor deposition (pinpoint CVD) technique using the electron beam of SEM(scanning electron microscope) to generate a carbon nanowire in a desired position under observation.

2 Concept of pinpoint CVD

It is known that when the electron beam of SEM is irradiated to an object, the residual-gas molecules near the object (mainly consist of carbon, hydrogen, oxygen) is excited and dissociated, and the dissociation is deposited on the object[3][4]. We applied this phenomenon to generation of the nanowire of free form in the air within a field perpendicular to the beam by scanning the electron beam from an object to the air slowly. Furthermore, 3-dimensional wiring is also possible by tilting a sample stage of SEM[5].

To apply this carbon nanowire to electron devices, we measured its electrical property. We generated a nanowire between two electrodes with 2 μm of gap to measure its volume resistivity (Fig. 3), and acquired the voltage-current curves that Fig. 4 shows. Although a change with the passage of time considered to be based on moisture is large, the volume resistivity of the nanowire could be estimated at the order of 100 Ω m. The high resistivity of carbon nanowire generable now is considered to be because for it to be amorphous. TEM (transmission electron microscope) image of the carbon nanowire indicates that it is amorphous (Fig. 5).

In order to use for various nanometer-scale electronic devices, generation of the crystal carbon nanowire, such as SWCNT, multi wall CNT, and so on, is also required. These are generable by controlling generation conditions (atmosphere gas, a catalyst, decomposition energy). Energy of electron beam of SEM (about 30 keV) is already enough for decomposition however, and on the other hand, heating mechanism is required because a catalyst is not activated unless heated. Then, we add gas introduction equipment, catalyst substrate, and heating equipment to the SEM chamber to generate crystal carbon nanowires. We call such generation technique “pinpoint CVD”.

3 Design of equipment for pinpoint CVD

For pinpoint CVD, mechanisms to provide (1)source of carbon, (2)energy to decompose the carbon compound, and (3)heat to activate a catalyst are required. As above-mentioned, the electron beam of SEM is used as the mechanism to provide energy for decomposition of carbon compound, and the other mechanisms are attached to the SEM chamber (Fig. 6). A nozzle (stainless steel pipe of 80μm of bores) and a needle valve are prepared as a gas introduction mechanism, and ethanol gas is used as the source of carbon.

Since temperature enough to activate a catalyst is guessed more than about 600 degrees centigrade, it is important to protect SEM from thermal damage. The marginal temperature of objective lens of the SEM that we used (S-4000,by HITACHI Co., Ltd.) is 100 degrees centigrade, and the marginal temperature of the SEM stage is 60 degrees centigrade. Therefore, it is necessary to reduce the size of a heating part and

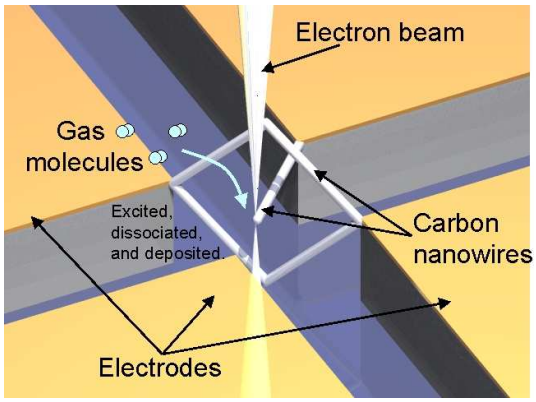

Fig. 1: Concept of pinpoint CVD

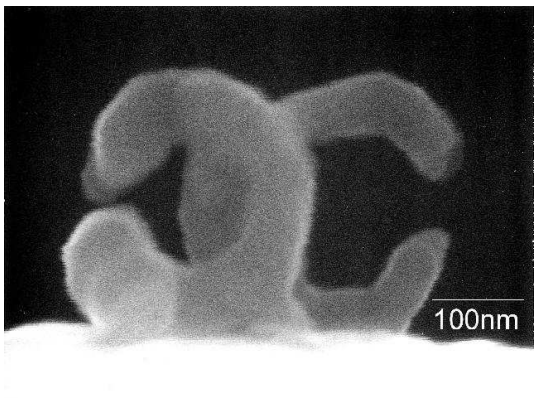

Fig. 2: Example of carbon nanowire

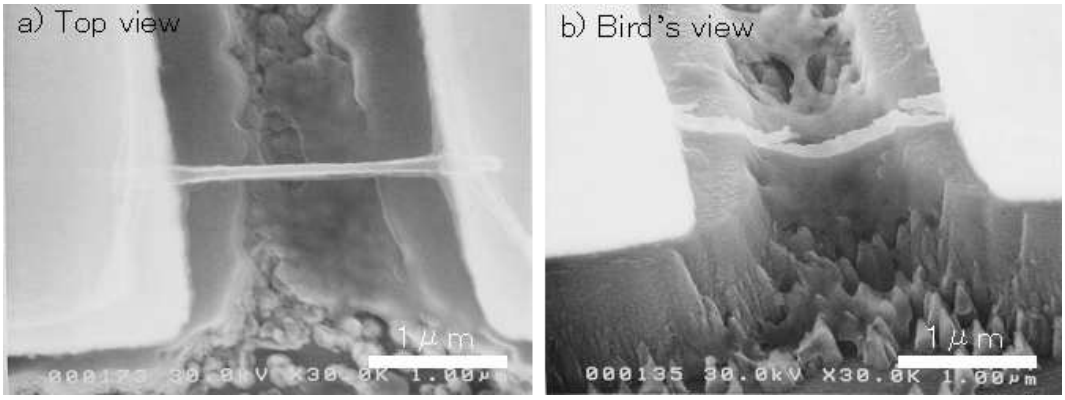

Fig. 3: SEM view of test chip for measurement of resistivity of carbon nanowire

the size of the contact section with the heating part as much as possible to decrease heat conduction, and reflecting plates are required to decrease thermal radiation. Then, the tungsten ribbon with the thickness of 25 micrometers, a width of 750 micrometers, and a length of 15mm was adopted as the heating part, and ceramic pipe(ϕ3mm,L=2mm) and ceramic adhesives were used for fixation of the heating part. In order to interrupt radiant heat, the stainless steel pipe of 5mm of bores and the stainless steel pipe of 9mm of bores have been arranged around the heating part, and two stainless steel plates with a thickness of 0.5mm and 50mm square have been arranged to each upper and lower sides of the heating part as reflectors. Fig. 7 shows schematic of heating unit, and Fig. 6 shows photographs of it. We used a zeolite as a catalyst, and applied it directly on the surface of the ribbon heater.

4 Experiment

Since the marginal degree of vacuum of the specimen chamber of SEM is about 6×10^{-2}Pa, the needle valve of an ethanol gas introduction mechanism is adjusted so that the degree of vacuum of the chamber may be set to about 5.2×10^{-2}Pa. Next, the current of about 2 A is impressed to the heater so that the temperature of a heater might turn into 500 degrees centigrades. However,the picture of SEM became unstable and CVD was not able to be performed. The cause is considered because temperature control of a heater is imperfect, a part of heater was overheated, and the detector of SEM was saturated with the thermoelectron from there. Therefore, positive thermo control of the heater and protection of the detector

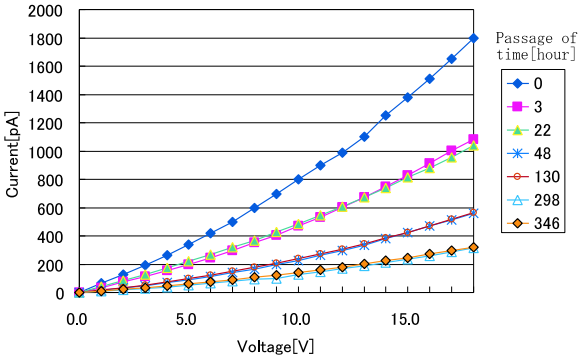

Fig. 4: Graph of voltage vs. current

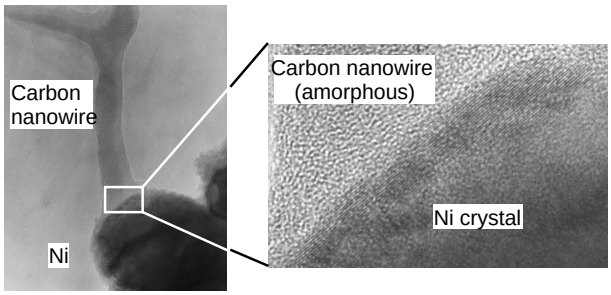

Fig. 5: TEM view of carbon nanowire on Ni substrate

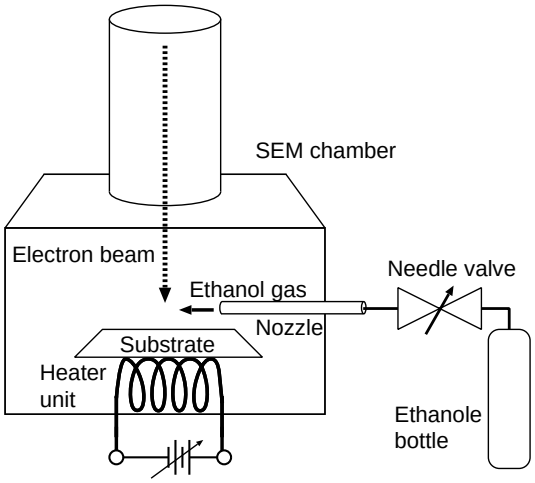

Fig. 6: Schematic of equipment for pinpoint CVD

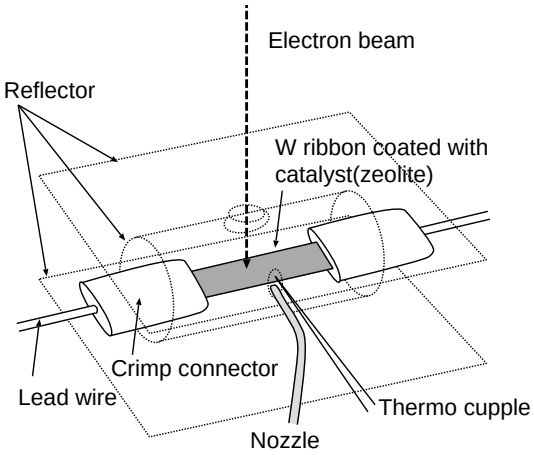

Fig. 7: Schematic of heating unit

are future subjects.

Next, we tried the experiment for applying amorphous carbon nanowire to an electron device. Because the amorphous carbon nanowire has large resistance compared with a single wall carbon nanotube(SWCNT) which conventionally used for research of single-electron devices or wiring, this nanowire is considered to be suitable for the device which operates by electric fields, such as field emission device. As an example, the nano vacuum tube with 500nm gapped electrodes was made (Fig. 9), and durability of the nanowire was evaluated. The breakdown test was performed having applied the voltage of about 50 V, and the result indicated that the nanowire has higher durability than an Au metal thin film of 50nm in thickness. We plan to measure the electric discharge efficiency of a nanowire and to control of the nano vacuum tube by electric field from now on.

5 Conclusion

We developed “pinpoint chemical vapor deposition” technique using the electron beam of SEM(scanning electron microscope) to generate a carbon nanowire in a desired position. Since the carbon nanowire gener-

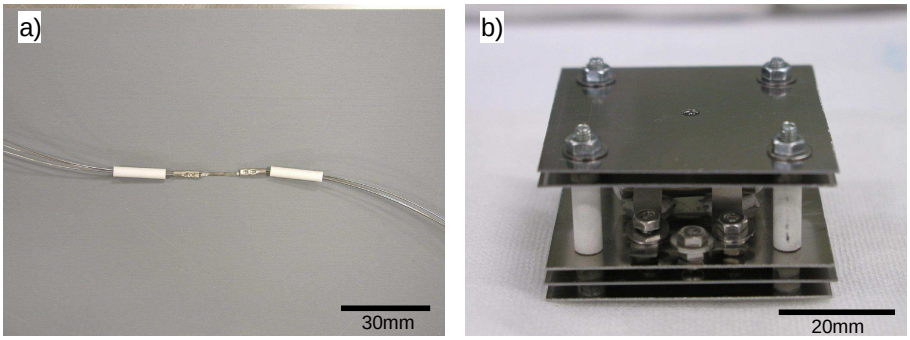

Fig. 8: Photographs of heater: a)Heating part, b)Reflectors

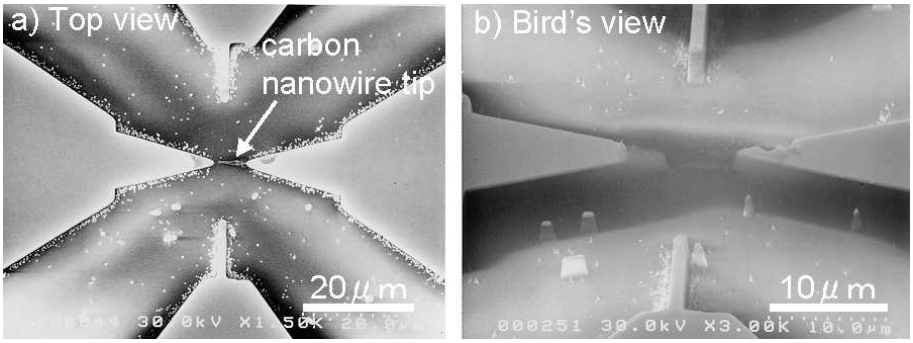

Fig. 9: Example of field emission device(SEM view)

ated using the residual gas in SEM as a source of carbon was amorphous, we made ethanol gas introduction equipment and catalyst heating equipment, and attached them in SEM. Although the experiment which generates a crystalline nanowire using the equipments was carried out, generation of a nanowire couldn't be performed because of the thermoelectron from a heater. Protection of the detector of SEM from the thermoelectron and positive temperature control are performed, and the conditions which generate a crystalline nanowire will be investigated from now on.

References

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