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A Study Of Carbon Nanotube-Based Ionization Gauges

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Abstract

Low-pressure detection technology utilizing the field emission of carbon nanotubes (CNTs) is introduced. The use of an ionization gauge is a viable alternative method for measurements at low pressure levels, but their use is limited by such factors as the bulky size, high power consumption, x-ray radiation, heat and light generation, and outgassing associated with this type of gauge. To overcome the limitations of conventional ionization gauges, CNTs have been proposed as an electron source. The performance of a CNT-based low-pressure gauge, including the sensitivity, measurement range, and linearity, has been improved greatly by changing the structure of the electrodes. The sensor showed a linear pressure measurement range from 5□10-7 to 10-2 Torr. Furthermore, the service life of the CNT emitter could be extended greatly by modulating the pulse of the voltage with a 20 % duty ratio. However, the service life of the CNT-based sensor is especially short, particularly when it is used at relatively high pressure levels. Accordingly, a CNT array directly grown by thermal Chemical Vapor Deposition is proposed. An integrated emitter directly grown with a catalyst metal can provide a low turn-on field by reducing the distance between the grid and CNTs while providing a longer emission lifetime. The characteristics of the directly grown CNT array and the screen-printed CNT array are compared for possible use with a practical pressure sensor.

Keywords: Field emission, Carbon nanotube, Ionization, Pressure

1. Introduction

Many applications utilizing the Carbon Nanotube (CNT), which was developed in 1991, have been studied. As CNTs have a high aspect ratio and a sharp tip, they are an excellent material for field emissions. In addition, it has been proposed that cold electrons emitted from CNTs can be used for the detection of low pressure in the range of 5x10-7 ~ 10-2 Torr. A CNT emitter provides many advantages compared to conventional ionization gauges, such as a small size, the absence of outgassing, and no generation of heat or light [1]-[4].

A CNT-based ionization gauge has a structure that is similar to a field emission display (FED), which has a low turn-on voltage and features both the advantages of a cathode ray tube and a plasma display panel. The potential power of the field emission display was determined theoretically in 1958, and Spindt manufactured an emission element with micro-tips fabricated by MEMs in 1968. At present, CNT is considered a powerful alternative for efficient field emission. The structure of a

CNT-based ionization gauge is similar to that of FED, but requires a different voltage combination in order to obtain a stable ion current [5]-[7].

A cost-effective device was developed by the authors using a screen printing method. However, the screen-printed array had a degradation problem, which meant that it was not feasible for long-term measurements. The lifetime of the device could be improved by applying a pulse-width modulation (PWM) signal, however, the device remains limited in terms of measurements in the high-pressure range.

On the other hand, a directly grown CNT array is known as a stronger emitter capable of long-term stability, although it is not easy to manufacture a large-area array. Thermal chemical vapor deposition (Thermal CVD) and plasma enhanced chemical vapor deposition (PECVD) can be used for the vertical growth of CNTs.

In this paper, improved performance of an ionization gauge with a screen-printed array is presented. Additionally, the characteristics and fabrication process of an integrated emitter are proposed for use in a pressure sensor.

2. Performance Improvement Of Screen-Printed Array Sensor

The screen-printing method is an easy and efficient way to manufacture the field emission source. The preliminary results of a low pressure sensor with screen-printed CNT array were reported in [3] and [4]. As discussed in those studies, a degradation problem was the most serious defect in the screen printing method, since the CNT was damaged by returned electrons. Fig.1. shows a schematic diagram of the modified structure in which electrons and ions are trapped by a second grid. This is similar to a Bayard-Alpert gauge. It consists of a CNT array from which cold electrons are emitted, a first grid to induce electron emission and accelerate it, a second grid in which electrons are trapped, and a collector where the ion current is collected. One or two collectors are surrounded by the second Grid. The CNT array was fabricated by the screen printing method. In order to improve the emission efficiency, a mechanical surface treatment with vinyl tape was carried out. This fabrication process is explained in [3] and [4].

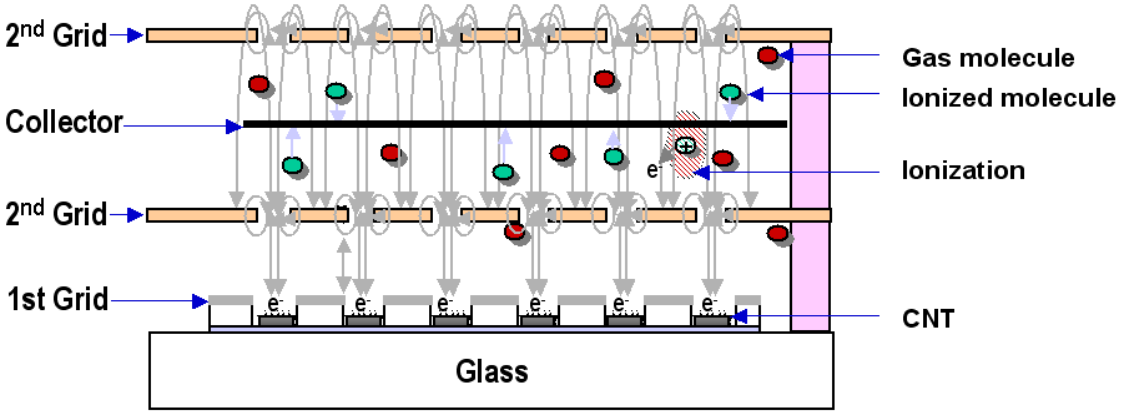

Figure 1. Schematic diagram of a modified CNT-based ionization gauge

Potentials applied to electrodes should be specially arranged as follows for the detection of pressure change. The potential of the first grid, Vg, should be high enough to induce the field emission compared to the potential of the CNT array electrode (base electrode), Vs. The potential difference depends on the characteristics of the CNT array, but it should be greater than 170 V for the screen-printed array. If the gap between the CNT array and the first grid is decreased using an integrated fabrication process, the turn-on voltage may be reduced to approximately 50 V. The potential of the second grid, Vg', should be higher than the potential of the first grid in order to accelerate the electrons. The potential difference between the first and the second grids should be changed according to gases used in a vacuum chamber, as gas molecules have a optimum ionization energy. Finally, the potential of the collector, Vc, should be lower than the potential of the second grid in order to collect ionized molecules. Typical potential combinations are given in Fig.2, which shows the pressure characteristics in log-scale, when the emission is induced by DC voltage applied to the first grid.

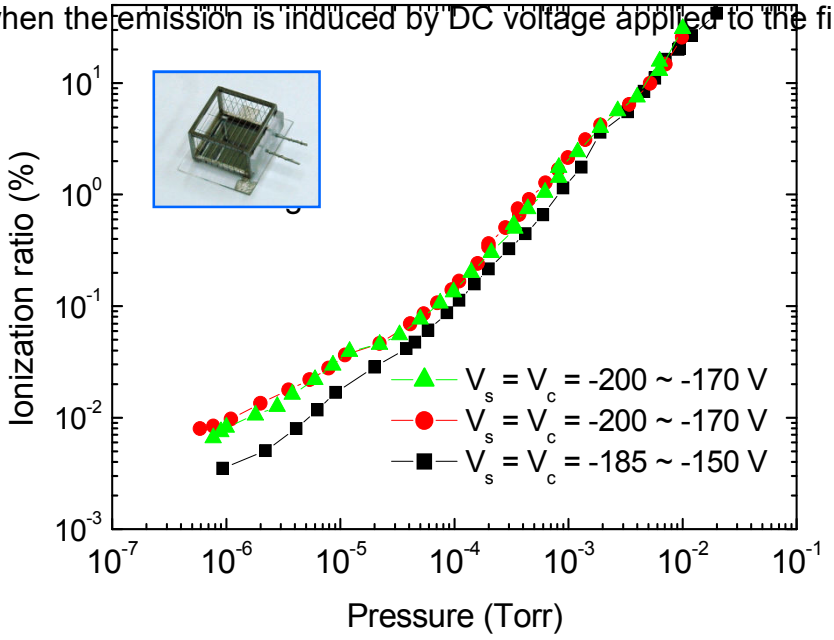

Figure 2. Pressure characteristic when driven by DC voltage

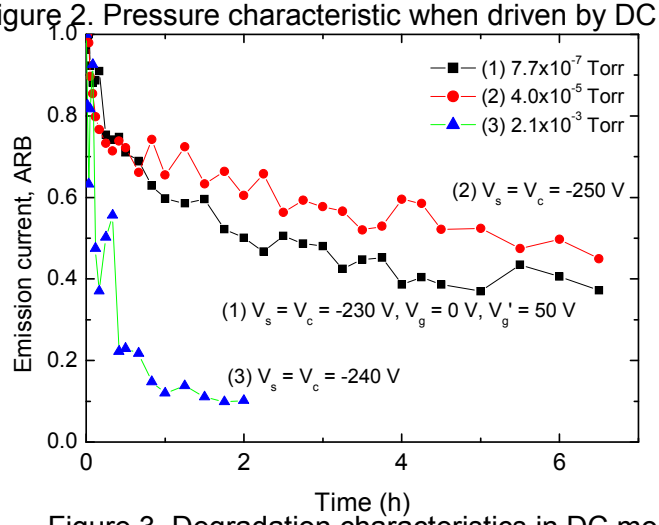

Figure 3. Degradation characteristics in DC mode

The emission current from the CNT array should be changed according to the pressure, because more electrons are required to increase the ionization probability at a low pressure. The ratio of the collector current to the emission current shown in Fig.2 is repeatable when the potentials of the electrodes are identical. However, if different voltages are applied, the sensitivity changes, as the ionization efficiency changes according to the electron energy.

As mentioned earlier, the fabrication of the CNTs emitter is very easy when using the screen printing method. However, the most critical problem is a significant degradation as shown in Fig.3. In DC mode, the emission current decreased to 40 % ~ 60 % of the initial current value, and then stabilized. Also, the emission current degraded to nearly 10 % within two hours at a high pressure over 10-3 Torr.

There are possible causes for this degradation. The first is that the gas molecules ionized in between the first and the second grid may return to the CNT array and damage it, even when the gap is small enough to reduce the probability of ionization. The second is that CNTs can be burned by the oxygen remaining in the vacuum chamber. The third possible cause is that CNT can break and disappeared under a high electric field. The first is most likely, the other causes are well known in the FED area, but require further investigation.

Fig.4 shows the degradation characteristics when PWM signals instead of DC voltage are applied to the first grid. As the PWM has a smaller duty ratio, higher voltage should be applied to obtain the same emission current. When the duty ratio is 80 %, the amount of degradation was similar to the experimental result in DC mode. The degradation decreased according to the duty ratio. In the case of a 20 % duty ratio, the emission current increased rather than decreased over time. However, this experiment was carried out under high vacuum conditions below 10-6 Torr. If the pressure is relatively high, the emission degrads rapidly even in PWM mode.

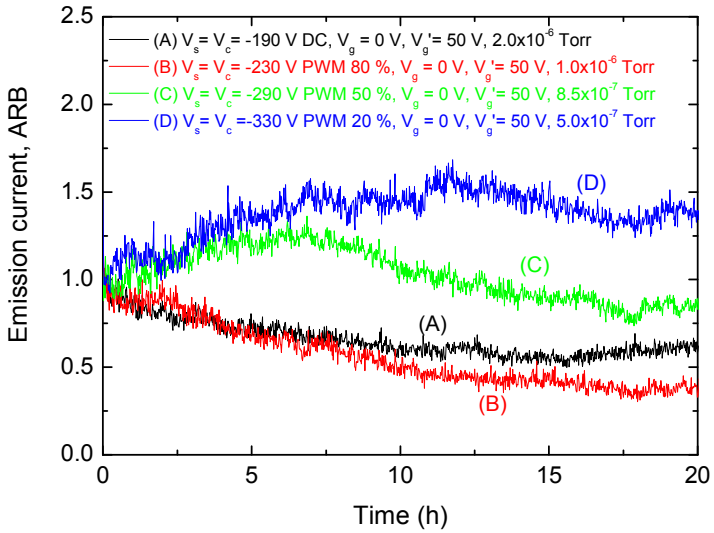

Figure 4. Degradation characteristics in PWM mode

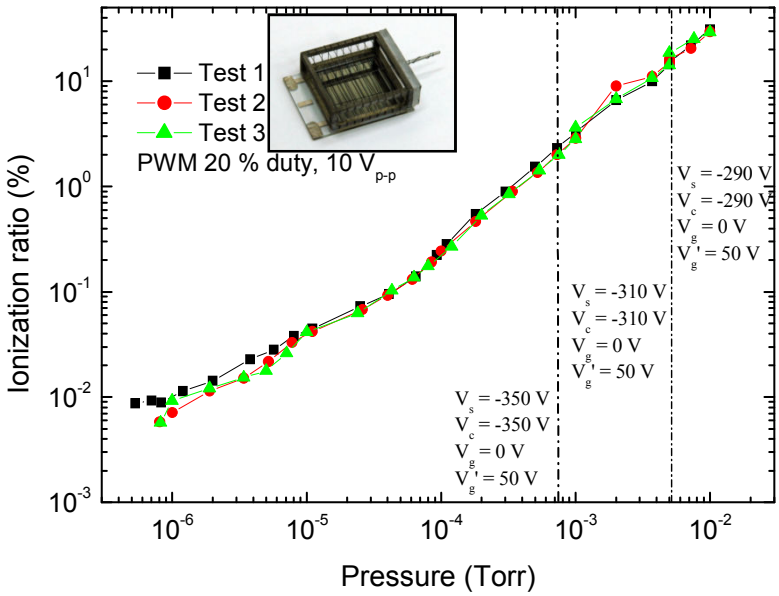

Figure 5. Pressure characteristics when driven by PWM

Fig.5 shows the pressure characteristic when driven by a PWM signal with 20 % duty ratio. It has good repeatability and linearity, as in the measurement result in DC mode shown in Fig.2.

If the pressure is increased up to 10-3 Torr, the significant degradation that occurred in DC mod occurs as well in PWM mode. In order to obtain a stable emission current, the pressure should be kept at a minimum of 10-5 Torr or below. In order to solve the degradation problem, the measurement range should be adjusted to a higher vacuum. In this case, a high emission current is required to increase the probability of ionization, but the high potential required for a high emission current is related to the ionization efficiency of gas molecules. Eventually, the turn-on voltage should be reduced to obtain a sufficient number of electrons with the proper electron energy.

However, the screen printing method is limited when reducing the turn-on voltage, as it is difficult to reduce a gap between the CNT array and the first grid, which is currently 200 □m. The direct growth method can serve as an alternative to reducing the gap, and thus, the turn-on voltage. Moreover, directly grown CNTs are known to be stronger than screen-printed CNTs. If the emitter is fabricated in a MEMs process, CNTs can be grown directly by thermal CVD with a catalyst metal, and the gap can be reduced to less than 10 □m.

3. Directly Grown CNT Array Sensor

3.1 CNT Growth by Thermal CVD

Directly grown CNTs by thermal CVD and PECVD have been studied for the characteristic of high efficiency. This fabrication process is well established. Although it is difficult to create an array with a large area using the direct growth

method, but it is sufficient for the pressure application. To compare a directly grown CNT array with a screen-printed array, the CNTs in Section 2 was replaced with thermally grown CNTs.

Thermal CVD or PECVD uses catalyst metals such as Ni, Co, or Fe to grow vertically aligned CNTs. In detail, 100 nm of Ti is deposited onto a Si(100) wafer using an E-beam evaporator. 7 nm of Ni is then deposited onto the Ti. The thickness of the catalyst metal is related to the diameter of the CNTs.

The CNT growth process was carried out under a variety of conditions that included different temperatures, metal deposition times and inert gases. Fig.6 shows the thermally grown CNTs. Acetylene (C2H2) gas was used for the growth of CNTs.

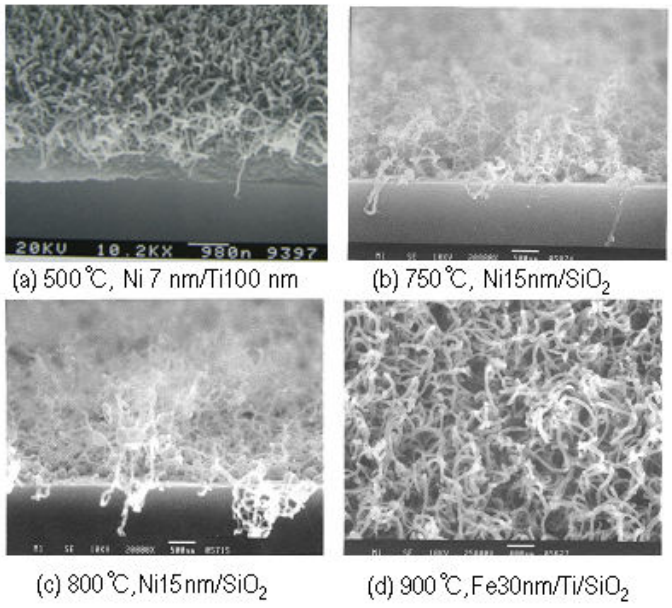

Figure 6. SEM image of CNT growth

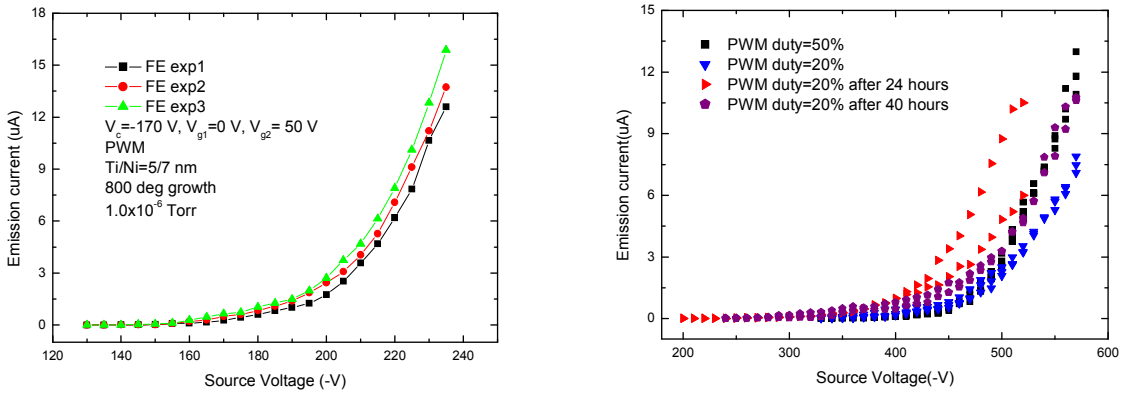

Figure 7. Field emission characteristics of a triode CNT array

At low temperatures, CNTs were more vertically aligned than at high temperatures. However, CNTs grown at high temperatures had a lower turn-on voltage compared to those grown at a low temperature, although this was not

superior to those grown using the screen printing method. When grown at low temperatures, nano-fibers rather than CNTs could be grown. This should be verified using transmission electron microscopy.

The first grid used in the screen printed array was loaded onto the directly grown CNT pattern, which has a structure identical to that of the device in Section 2. Fig.7 shows the field emission characteristics of the triode CNT array, which was grown thermally. The thermally grown CNT array showed performance characteristics that were nearly identical to those of the screen-printed array in DC mode. Moreover, the efficiency was increased slightly as time passed. In PWM mode, the turn-on voltage was much higher than in DC mode. Moreover, the emission current was not stable with respect to emission time; however, it increased slightly.

3.2 Fabrication of an Integrated CNT Emitter

In order to obtain a sufficient high emission current at a low voltage, it is necessary to fabricate an integrated CNT emitter. Fig.8 shows the fabrication process of the integrated CNTs emitter.

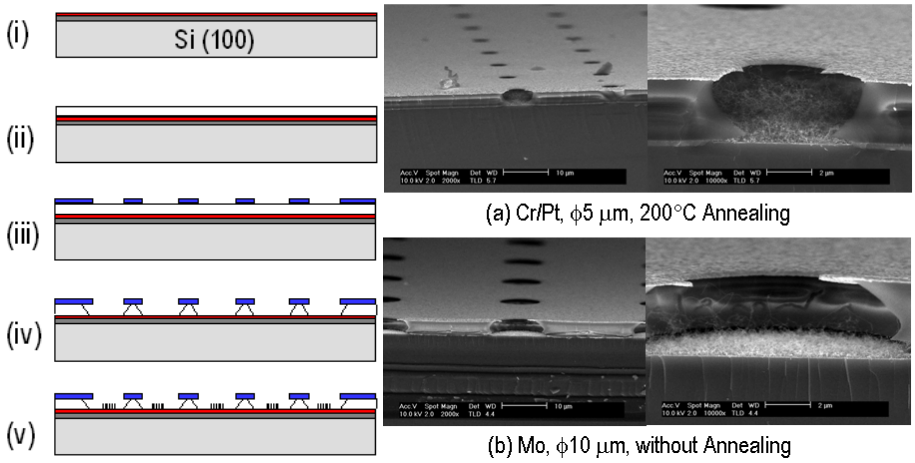

Figure 8. Fabrication of a triode CNT emitter of a pressure Sensor

Both Ti (100 nm) and Ni (7 nm), were deposited onto a Si(100) wafer as an electrode and a catalyst, respectively in step(i). SiO2 with a thickness of 3 ~ 5 □ were deposited at 450 □C by PECVD for insulation in step (ii). The SiO2 thickness is related to the turn-on voltage, as it determines the gap between CNTs and the first grid. If the thickness is thin, a low turn-on characteristic may result; however, it is difficult to control the length of CNTs, which should not reach the first grid. In step (iii), a hole array was patterned using a photo-lithography process. Either Cr/Pt (35/165 nm) or Mo was then deposited using an E-beam evaporator. The hole pattern was then completed by a lift-off process with a buffered oxide etchant. In step (iv), an undercut was formed by a wet-etching process and in (v), CNTs were grown by thermal CVD.

During the aforementioned processes, the hole array pattern was destroyed due to the residual surface stress difference of the Cr/Pt. This resulted from the temperature difference among the above processes. This problem can be solved if an annealing process is added or when ductile materials such as Au are used for adhesion between SiO2 and the other metals. The specimen before the etching process, step (iv), was annealed at a high temperature range from 100 □C to 800 □C for 20 min. When annealed at high temperatures greater than 800 □C, the pattern was stripped off during the wet-etching process. In addition, an annealing effect was not obtained at 100 □C.

When Mo instead of Cr/Pt was deposited by sputtering, an annealing process was not required as Mo is stronger and more adhesive compared to other materials. However, it was difficult to control the hole diameter using Mo.

When CNTs were grown thermally after an annealing process at high temperatures, the surface of the first grid was damaged. This was not a critical problem, but the annealing time should be controlled to minimize this type of damage.

Figs. 8(a) and (b) show the integrated emitter with a Cr/Pt and Mo grid, respectively, fabricated by direct CNT growth.

When a fabricated wafer was diced after all of above processes, a contact problem was found to exist between the base electrode and the first grid. This may have resulted from the excessively grown CNTs, but it appears to have resulted from grid damage due to sawing. Laser cutting is an option that may avoid this problem, but this process was excluded on account of the high cost associated with it. Instead of laser cutting, an additional mask that removes the base electrode underneath the sawing position should be designed before the process in step (i) in Fig.8.

4. Conclusions

Two methods are currently used to manufacture CNT-based pressure sensor. A screen printing method has a low turn-on field, but also, has a serious degradation problem. A modified sensor showed a linear pressure measurement ranging from 5x10-7 Torr to 10-2 Torr. Moreover, the service life can be improved by applying PWM signals to the sensor. A direct growth method by thermal CVD is not efficient for field emission compared to a screen printing method, but it is possible to reduce the gap between the CNT array and the first grid significantly. The integrated emitter is expected to have a low turn-on field and a long service life.

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