Growth of Carbon Nanotubes on Anodic Aluminum Oxide Templates: Fabrication of a Tube-in-Tube and Linearly Joined Tube

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Received December 19, 2000. Revised Manuscript Received March 15, 2001

We have fabricated multiwalled carbon nanotubes (CNTs) with flowing acetylene, using a well-ordered porous anodic aluminum oxide (AAO) nanotemplate with or without deposition of Co in the pores as a catalyst. Without deposition of Co, the tubes were made in the pores having the shape of the pores by catalysis with the alumina of the AAO templates. With deposition of Co, both alumina and Co could work as a catalyst. By widening the pores after Co deposition, tubes grow out from the pores, by forming a tube-in-tube, which could be used for electrochemical energy storage. Since the alumina of the AAO templates works as a catalyst, one can fabricate special shapes of CNTs by designing the pores of AAO templates. We have succeeded for the first time to fabricate linearly joined CNTs by using AAO templates prepared by using pore widening and multianodization techniques. The electronic properties of the linearly joined CNTs will be affected critically by the junctions that contain five- and seven-membered carbon ring defects and could be controlled by changing the ratio of the two diameters of them. A schematic to fabricate FET (field-effect transistor) using the linearly joined CNTs fabricated on AAO templates has been suggested.

Introduction

Carbon nanotubes[1] (CNTs) have generated a great deal of interest because of their extraordinary mechanical[2,3] and electronic[4−6] properties. Well-ordered CNT structures[7−9] are of great importance for technical applications such as cold-cathode flat panel displays. Porous anodic aluminum oxide (AAO) templates prepared by a two-step anodization process[10] has been used for fabrication of highly ordered CNTs.[7] The nanotubes were very uniform in diameter, highly ordered, and perfectly vertical with respect to the plane of the template. In fabrication of CNTs using AAO templates prepared by a one- or two-step anodization process, Co was deposited in the bottom of the pores of AAO templates as a catalyst.[7,11,12] CNTs were made only in the pores for most cases[7,11] but sometimes grew out from the pores.[12] The condition is not known to grow CNTs out from the pores. Some evidence that alumina of AAO templates works as a catalyst has been found. Kyotani et al.[13] have fabricated CNTs on aluminum oxide membrane without deposition of Co, and Suh and Lee[7] have found that CNTs fabricated on the AAO templates have slightly widened top tips that reflect the surface structure of the template. These could be possible when the alumina of the template works as a catalyst in the fabrication of CNTs. If alumina works as a catalyst, Co and alumina will compete with each other as a catalyst in the fabrication of CNTs using AAO templates.

The electronic properties of linearly joined tubes have been studied theoretically.[14] By calculations, the pair of armchair and zigzag nanotubes joined linearly is expected to exhibit rectifying behavior. Experimentally, this kind of behavior has been observed for joined single wall tubes but not those linearly joined.[15] A linear junction of two tubes with different diameter consists of 5- and 7-menbered rings.[14,15] These rings act as defects and decrease the conductivity of the joined tube. Therefore, by joining CNTs of different diameters one

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10.1021/cm0014076 CCC: $20.00
Published on Web 06/22/2001

can modify the electronic characters of CNTs. CNTs fabricated on AAO templates are known to be multi-walled tubes,[11] which can be metallic or semiconductors, depending on their diameters and the chiralities of the outer shell.[16] If alumina of AAO templates works as a catalyst and tubes are made in the pores with the pore shape, we can fabricate special shapes of CNTs by designing the pores of AAO templates. By making linearly joined tubes, one can modify the electronic properties of them. In this case, linearly joined CNTs could also be used in fabrication of nanoscale electronic devices such as a field-effect transistor (FET). So far, semiconducting single-wall carbon nanotubes have been considered as a proper material for fabrication of FET using CNTs.[17−19]

Here, we have studied the fabrication of CNTs using AAO templates, with and without deposition of Co into the pores, with flowing acetylene, and made a tube-in-tube and linearly joined CNTs.

Experimental Section

A high-purity aluminum sheet (99.999%, 0.5 mm thick) was used as a substrate material. It was electropolished in a solution of perchloric acid and ethanol to a mirror finish. Clean aluminum sheets were anodized in a 0.3 M oxalic acid solution at 17 °C at a constant applied voltage of 40 V for 24 h. The resultant aluminum oxide film was subsequently removed by dipping the anodized sheet into an aqueous mixture of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C. A second anodization was performed for 20 min under the same condition as the first one. For some templates, a voltage drop from 40 to 20 V by 5 V steps was done at the end of the second anodization. The pore depth was about 2 μm. The pores of the template prepared without a voltage drop were widened by dipping the material into an aqueous 0.1 M phosphoric acid solution for 40 min. For fabrication of linearly joined tubes, a third anodization was done under the same condition as the first one after the pore widening. Co was deposited in the bottom of the pores of templates prepared with a voltage drop as a catalyst and then etched in 0.1 M NaOH solution for 3 min at room temperature.

CNTs were fabricated in the pores by following a published method.[7,11] After placing the template in a tube furnace, acetylene was pyrolyzed to form CNTs by flowing a mixture of acetylene and nitrogen at 700 °C for 20 min. Fabricated templates and CNTs were analyzed by using scanning electron microscopy (SEM; Philips FEG XL, 30 kV and Hitach S-4500) and transmission electron microscopy (TEM; JEM-2000EXII).

Results and Discussion

Figure 1a shows a SEM image of the AAO template surface after the second anodization and pore widening processes. The nanopores of a uniform size exhibit a perfect 2-D array with a hexagonal pattern. The average diameter and interpore distance are 43.8 ± 0.8 and 104.2 ± 2.3 nm, respectively. The pore density is about 1.1×10^{10} pores/cm^2. It is clearly seen that the mouth of the pores is widened like a funnel. The arrays of pores are not perfect in a large area. In a lower magnification image, it has been found that defects in pore arrays occur at domain boundaries. The domain sizes were 3−4 μm. Figure 1b shows a SEM image of the bottom part of the CNTs grown on a template whose pores were widened and pore depth was about 2 μm, without deposition of Co into the pores as a catalyst. To examine the bottom part of the nanotubes, we removed the Al layer by dipping the sample into a saturated $HgCl_2$ solution, and then we mechanically polished the bottom oxide partially with alumina powder and etched the oxide in phosphoric acid. In Figure 1b, some tubes are slightly tilted during sampling by bending the template and then etching away oxide. Before etching away oxide, the nanotubes were well-ordered and perpendicular to the template. The tubes are highly uniform in diameter with an average of 50.0 ± 0.7 nm. The average diameters measured at the top and bottom parts of tubes were even within measuring error. It is clearly seen that the bottoms of the tubes are closed, whereas the bottoms of the tubes[7] were opened when Co was deposited. This is not strange because the bottoms of the pores without deposition of metals have a hemisphere shape and the closed nanotubes will be made naturally when carbon nanotubes are formed on the inner surface of the pores. The closed bottoms and slightly widened top tips[7] of the tubes are strong pieces of evidence of that the tubes are made on the inner surface of the pores in the shape of the pores by catalysis with the alumina of the AAO templates.

No tubes were grown out from the pores. This may give a clue to understand the growth mechanism of the tubes made on the inner surface of the pores by catalysis

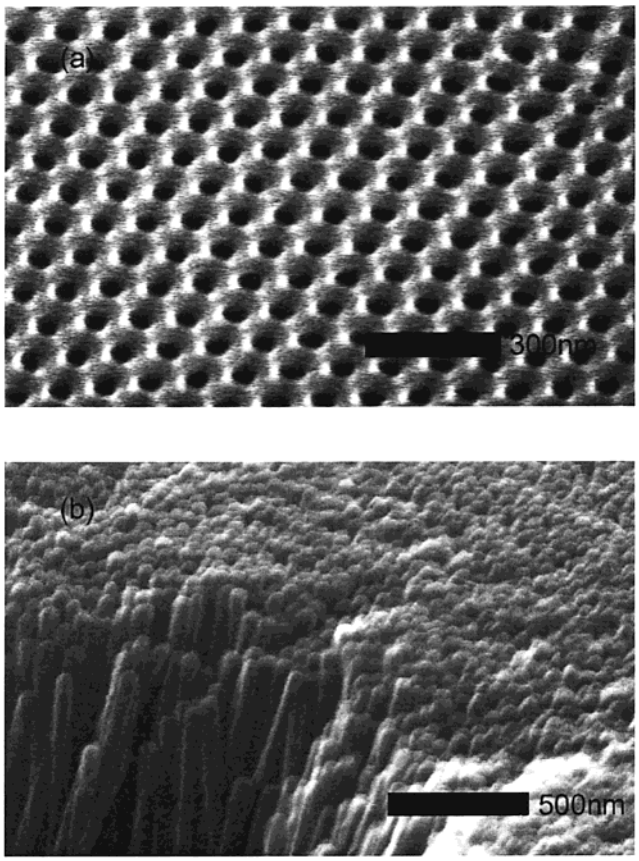

Figure 1. SEM images of (a) the surface of an AAO template after the second anodization, (b) the bottom of CNTs made in the pores of a template, without deposition of Co, after removing all Al metal and oxide including the bottom oxide.

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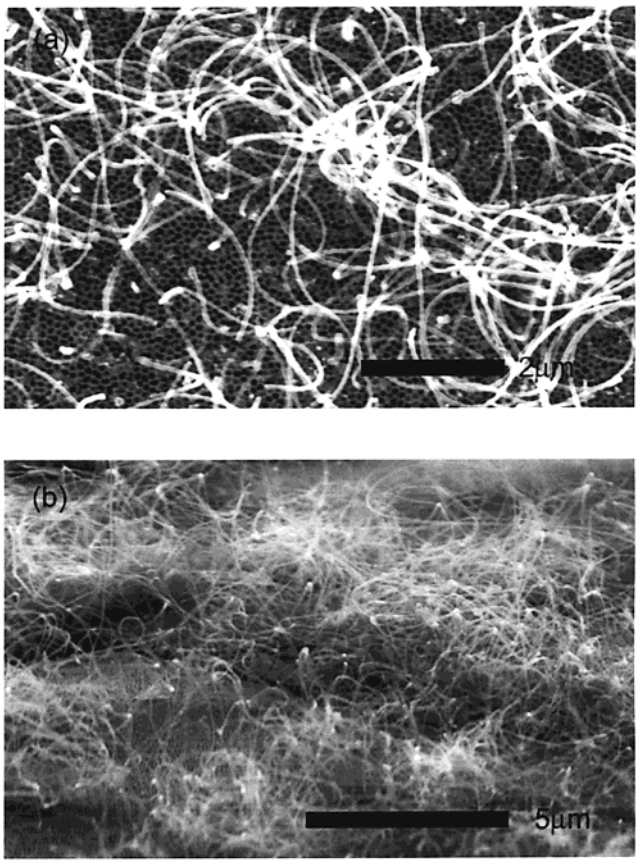

Figure 2. SEM images of CNTs grown out from the pores of AAO templates in which Co was deposited and then were widened in NaOH solution: overviews of the templates whose pore depth to Co were (a) 600 nm and (b) 400 nm, without any treatment.

with the alumina of the AAO templates. Since the alumina of the AAO templates works as a catalyst, carbonization will take place simultaneously on all the inner surfaces of the pores and the concentration of carbon will be very uniform on the entire inner surface of the pores. In this case, the entire shape of each tube will be formed simultaneously on the inner surface of the pores, not growing from any particular site or location. Therefore, the tubes could not grow out from the pores.

Figure 2 shows SEM images of CNTs grown out from the pores of templates in which Co was deposited and then were widened by etching in NaOH solution. The pores were widened uniformly and the average diameter of the pores was about 88 nm. There is no doubt that tubes are grown out from pores because one can see that the root of some tubes is in the pores (see Figure 2a). Tubes are curved and some of them are very long, longer than 10 μm. The diameter of the most tubes is about 60 nm, bigger than that of Co nanowires, about 29 nm. The diameter of the CNTs grown out from the pores was affected by the percent of acetylene in the mixture of acetylene and nitrogen gases. The diameter was about 40 and 60 nm when using gas mixtures of 5 and 10% acetylene, respectively. The density of the tubes grown out is higher in Figure 2b than 2a. Two samples were prepared under the same conditions, except the amount of Co deposited. The pore depth to Co in the samples for parts a and b of Figure 2 was about 600 and 400 nm, respectively. The number of tubes grown out from

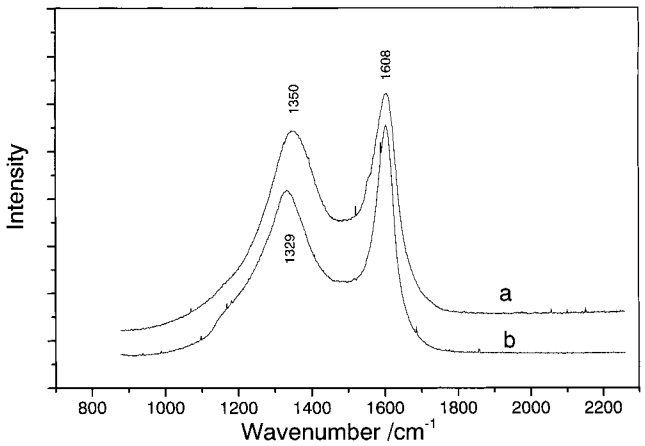

Figure 3. Raman spectra of CNTs (a) formed in the pores, without deposition of Co into the pores of an AAO template and (b) grown out from the pores deposited with Co, excited with 514.5 nm.

the pores was increased upon decreasing the depth of the pores to Co. It is clear that the tubes grown out from the pores are made by using Co as a catalyst, since the tubes made by catalysis with alumina are made only on the inner surface of the pores without growing out.

The Raman spectra of CNTs formed in the pores (a) and grown out from the pores (b) are compared in Figure 3. There are two strong bands near 1340 and 1608 cm^{-1} in both spectra. The former is known to be due to defect or carbonaceous particles on the surface of the CNTs and the latter is known as the G line.[20,21] For most tubes fabricated by chemical vapor deposition (CVD), the former is broader and stronger than the latter.[21] For well-graphitized cases, the former is weak or almost disappears and the latter is very narrow and the strongest.[20,21] The frequency of the band near 1340 cm^{-1} is not the same in both spectra. For the CNTs grown out from the pores, the frequency is slightly downshifted compared to that of CNTs formed in the pores. The band at 1608 cm^{-1} is relatively more narrow and intense for the CNTs grown out than those formed in the pores. This may mean that the CNTs grown out from the pores, with deposited Co as a catalyst, is better graphitized than the CNTs formed in the pores, without deposition of Co.

When CNTs are fabricated on AAO templates with deposition of Co into the pores, alumina and Co will compete with each other as catalyst. Since the tubes made on the inner surface of the pores of the AAO templates are known as multiwalled tubes,[11] the number of walls will be increased with time. Consequently, the inner diameter of the tubes forming on the inner surface of the pores will be decreased with time. With pore widening after Co deposition, the CNTs are grown out from the pores and the diameter of the CNTs grown out from the pores is bigger than that of Co nanowires. The latter corresponds to the diameter of the pores where Co has been deposited. Therefore, no tubes whose diameter is bigger than that of the Co nanowires can grow out from the pores without pore widening after Co deposition. It should be mentioned that in some

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samples few tubes were grown out from the pores without pore widening after Co deposition, but the diameter of the tubes was much smaller than that of the Co deposited. Also, tubes were grown out from the pores without pore widening after Co deposition when the depth to the Co deposited was very shallow. By etching with NaOH after deposition of Co, the part of each pore where no Co was present would be widened. In Figure 2, the diameters of the pores and the tubes grown out are about 88 and 60 nm, respectively. Pore widening will provide some space for gas diffusion during growing tubes. The growing rate of the tubes will be affected critically by the gas diffusion to Co. If the pore diameter after pore widening is not big enough and the growing rate of the tubes made by catalysis of Co nanowires is not fast enough, they will be blocked by the multiwall nanotubes forming on the inner surface of the pores. Besides gas diffusion to the Co catalyst, there must be other crucial requirements to grow out tubes from the pores, because only a few tubes grew out even with pore widening.

One can consider two growth mechanisms,[22] the tip and root, for Co deposited in the pores. In the case of the root growth, the growing tube on Co deposited in each pore will block at least partially the gas diffusion to Co in each pore. If gas diffusion is blocked, the growing rate will be decreased. Consequently, the growing tube on Co will be blocked by the tube forming on the inner surface of the pore by catalysis of alumina and could not grow out from the pores. Therefore, the root growth may be unfavorable. In the tip growth, the gas diffusion will not be blocked since the growing site is at the top of the tubes. For the tip growth, Co could be carried to the top of the tubes during growing, but Co deposited in the pores is unmovable, almost fixed in the pores as long nanowires. A fragmented Co was included at the top tip of the tubes (see Figure 4a). This supports the tip-growth mechanism. To be carried to the top of the tubes, the long Co nanowires deposited in the pores should be fragmented and also the fragmentation should take place before being blocked by the tubes forming on the inner surface of the pores. This may be another crucial requirement to grow out tubes from the pores. The subsequent pore widening by NaOH after Co deposition will serve to loosen Co particles from the AAO wall in addition to pore widening, and Co could be fragmented relatively easily when carbon is dissolved. The growth mechanism should be studied more. Anyway, under the condition of pore widening after Co deposition, both Co and alumina could work as a catalyst. During the growth of the tubes by catalysis of Co, a tube with greater diameter would also be formed on the inner surface of each pore. This is called a tube-in-tube.

Figure 4 shows SEM images of tube-in-tubes fabricated using 5% acetylene after bending the template and then partially etched in NaOH solution. A TEM image of the top tip of a grown out tube is inserted. The number of tubes grown out is very small because the depth to the Co was relatively deep, about 1.5 μm. In Figure 4a, one can see clearly a tube-in-tube for which a smaller diameter tube is grown out from a larger one.

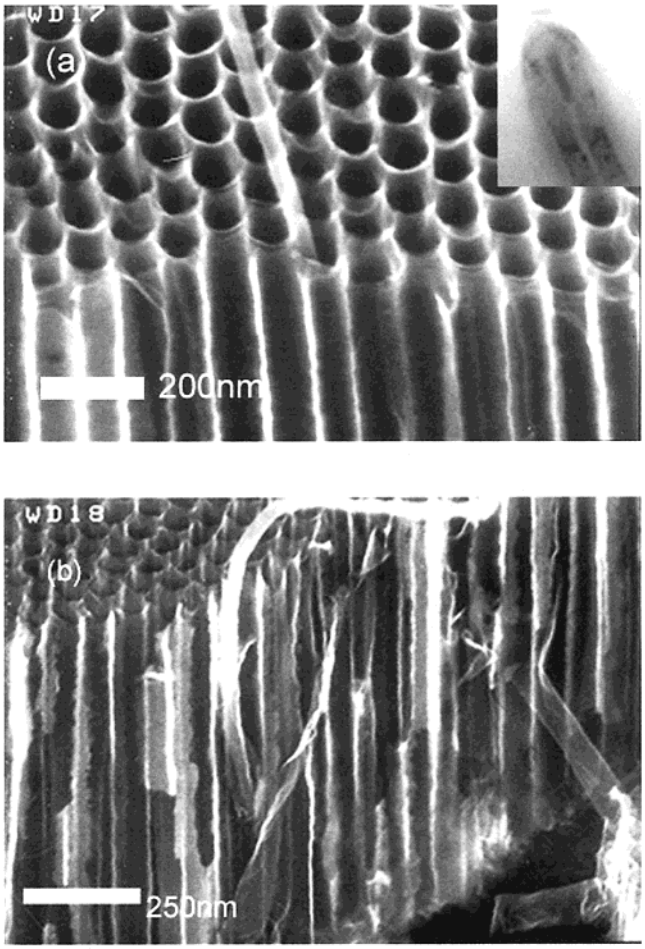

Figure 4. SEM images of tube-in-tubes after bending the template and then etched in NaOH solution. A TEM image of the top tip of a grown out tube is inserted. A piece of Co metal is included at the top tip of the tubes grown out from the pores, and the inner tube of the tube-in-tubes is straight.

At the top tip of the tubes grown out from the pores, a piece of Co metal is included. In Figure 4b, an inner tube is clearly seen where the outer tube has been broken partially. By carefully watching, one can see the remaining outer tube for which the oxide on the wall has been removed well. The diameter of the inner and outer tubes is about 37 and 68 nm, respectively. Both of the tubes are multiwalled and the wall thickness is 13 and 2 nm, respectively. This means that the tubes made on Co are much thicker than those made on alumina. The number of walls of the inner and outer tubes is expected to be about 38 and 6, respectively. A curled tube existing in a tube has been reported.[23] In our samples, the inner tube in a tube-in-tube is almost straight (see Figure 4b). Che et al. have suggested the possible application of a tube-in-tube in lithium ion batteries.[23] For this kind application, the conditions to form a tube-in-tube in every pore should be studied.

Since the alumina of the AAO templates works as a catalyst in fabrication of carbon nanotubes, one can fabricate special CNTs by designing the pores of AAO templates. CNTs having a special shape have been reported. Li et al.[24] have fabricated Y-junction CNTs

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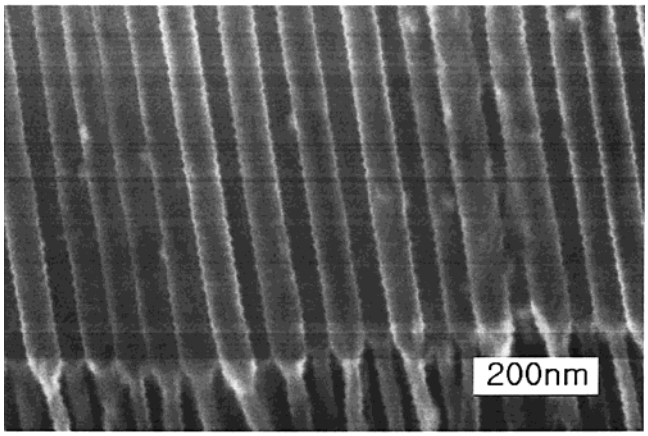

Figure 5. A SEM image of the linearly joined tubes fabricated on a well-ordered AAO template. The larger diameter is about 60 nm and the smaller one is 30 nm. Some tubes are slightly bent due to the alumina being etched away surrounding the tubes.

using a Y-branched nanochannel AAO template. Figure 5 shows linearly joined CNTs fabricated on an AAO template prepared by pore widening after a second anodization and then doing a third anodization. It is clearly seen that two tubes of different diameter are joined linearly. The larger diameter is 60 nm and the smaller one is 30 nm. Some tubes of the smaller diameter are bent. This is due to the alumina being etched away surrounding the tubes for observation of SEM images. The location and shape of the junctions are very uniform and the curvature of them is very smooth. The junctions contain five- and seven-membered carbon ring defects[14,15] and the electronic character of linearly joined CNTs could be affected critically by the ratio of the two diameters. The smaller diameter in the linearly joined tube is determined by the anodization conditions such as the electrolyte, voltage, and temperature of anodization,[25] and the larger diameter could be controlled within the interpore distance of the AAO template by changing the pore widening time.[26] Therefore, one could change the ratio of the two diameters in some range. Therefore, it may be possible to control the electronic properties of the linearly joined CNTs by changing the ratio of the two diameters.

Since the tubes are made in the pores that have a well-ordered hexagonal pattern (see Figure 1A), each linearly joined tube has six nearest neighboring tubes besides at edge and the tubes are surrounded by alumina that is an insulator. A schematic of the linearly joined tubes after milling the top and bottom of the tubes is shown in Figure 6. These linearly joined tubes could be used in fabrication of FET. As shown in Figure 6, if we connect one end of a CNT as the source, the other end as the drain, and one or some of the six nearest neighbors as the gate electrode, this is basically the same structure as an insulated gate FET. These linearly joined tubes are well-ordered, almost perfectly vertical with respect to the template plane, surrounded by insulate, and have a high density. Therefore, these linearly joined tubes could be used in fabrication of nanoscale electronic devices such as FET.

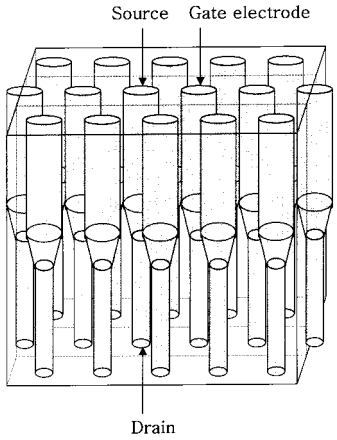

Figure 6. A schematic of the fabrication of a FET using the linearly joined tubes fabricated on an AAO template.

In conclusion, alumina works as a catalyst in the fabrication of carbon nanotubes using AAO templates with flowing acetylene. In the fabrication of CNTs with deposition of Co into the pores as a catalyst, both alumina and Co can work as a catalyst, but tubes can grow out from the pores only when Co works as a catalyst. To grow tubes out from the pores, the pores should be widened after deposition of Co. When both alumina and Co work simultaneously as a catalyst, a tube-in-tube is made. Since the alumina of the AAO templates works as a catalyst, one could fabricate special shapes of CNTs by designing the pores of the AAO templates. Using an AAO template prepared by pore widening after a second anodization and then doing a third anodization, we have fabricated linearly joined CNTs. These linearly joined tubes could be used in fabrication of nanoscale electronic devices such as FET.

Acknowledgment. This work was supported by the nanostructure technology project, the ministry of information and communication, and the National Program for Tera-level Nanodevices.

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