Synthesis of Nanostructured Hybrid between Carbon Nanotube and Inorganic Material towards Nanodevice Application

Mitsuhiro Katayama,* Shin-ichi Honda, Takashi Ikuno, Kuei-Yi Lee, Masaru Kishida, Yuya Murata, and Kenjiro Oura
Department of Electronic Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
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In this review, we demonstrate the device-oriented synthesis of carbon nanotubes (CNTs), by taking an energy storage device and a field electron emitter as examples. As one of the most desirable approaches to fabricating nanostructured hybrids between CNTs and inorganic materials, we present a method of coating carbon nanotubes with inorganic materials in multishell form, and its application to nanoprobe fabrication.

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I. INTRODUCTION

Carbon nanotubes (CNTs)[1] are state-of-the-art nanomaterials due to their unique physical and chemical properties [2]. To realize various applications of CNTs in nanodevices, the following are indispensable: (a) the device-oriented synthesis of CNTs, the morphology and structure of which are well-controlled; and (b) the fabrication of nanostructured hybrids between CNTs and inorganic materials such as metals, semiconductors, and insulators, and their interface control. For example, the following processes are necessary: (1) for nanoelectronics application, the reduction in contact resistance between CNTs and metal electrodes, high throughput process using self-organization, and fabrication of CNT-insulator composites, (2) for display application, the use of a highly efficient field electron emitter by controlled arrangement and low-temperature synthesis on a glass substrate with a large area, (3) for energy storage device application, the direct growth of CNTs with a long length and a high density on a metal substrate, and (4) for nanoprobe application, the control of contacts between CNTs and probes and electrochemical passivation.

In this review, we demonstrate the device-oriented synthesis of CNTs, by taking an energy storage device and a field electron emitter as examples. As one of the most desirable approaches to fabricating nanostructured hybrids between CNTs and inorganic materials, we present a method of coating CNTs with inorganic materials in multishell form, and its application to nanoprobe fabrication.

II. DEVICE-ORIENTED SYNTHESIS OF CARBON NANOTUBES

A. Towards Energy Storage Device

An electric double-layer capacitor (EDLC) is an energy storage device that utilizes an electric double layer formed on the interface between an electrode surface and an electrolyte [3]. EDLCs featured longer charge/discharge cycle life than that of secondary batteries. They are currently used as backup power sources for memories and have recently shown potential as a power source for electric vehicles. However, the energy density of EDLCs is lower than that of secondary batteries, thereby a higher capacitance is required. To date, due to their large effective surface area, CNTs have been proposed as electrode materials for EDLCs, instead of conventional electrode materials of active carbon [4–8]. However, the correlation between the morphology of CNTs and the performance of EDLCs using CNT electrodes has not been fully explored.

In this section, we describe the synthesis of vertically aligned CNTs with a long length and a high density on metallic substrates by thermal chemical vapor deposition (CVD) towards the electrodes of EDLC [9]. We fabricated an EDLC test device incorporating CNTs produced as electrodes, and investigated charge/discharge characteristics.

The thermal CVD apparatus is schematically shown in Fig. 1. The apparatus mainly consists of a stainless-steel nozzle for introducing carbon sources, and a tube furnace, and a metal substrate.
TABLE I: Growth conditions for long and high-density CNTs.

| Catalyst                  | Fe (5 nm) / Al (10 nm) |
|---------------------------|------------------------|
| Process to form
      catalyst nanoparticles | Annealing at 700 (60 min) |
| Growth temperature       | 550~700°C               |
| Deposition time           | 30 min                  |
| Source gas                | C₂H₂ 15 sccm            |
| Gas pressure              | 600 Pa                  |

FIG. 2: SEM image of catalyst nanoparticles for growth of long and high-density CNTs.

in which a sample holder is placed. The growth conditions are listed in Table 1. The base pressure was $10^{-3}$ Pa. Metallic sheets were used as substrates. Fe (5 nm) /Al (10 nm) multilayer thin films as a catalyst were deposited on the substrates using magnetron sputtering. The substrates were annealed in vacuum at 700°C in order to form catalyst nanoparticles, and then thermal CVD was carried out using acetylene gas under 600 Pa at 700°C.

We used the Fe/Al multilayer catalyst for direct growth of CNTs on metallic substrates for the following reasons. Figure 2 shows a scanning electron microscopy (SEM) image of the catalyst nanoparticles before the thermal CVD growth. It was found that the catalyst nanoparticles were uniformly dispersed with a number density of approximately $10^{10}$ cm$^{-2}$. Compared with the Fe catalyst, using the Fe/Al multilayer catalyst, the size distribution of the catalyst nanoparticles was narrow and the nanoparticles were small. The XPS spectrum of the sample indicated the formation of Al$_x$O$_y$ [10]. From this result, the catalyst nanoparticles array is likely to be formed as follows: (1) Al layers are oxidized by residual oxygen inside the furnace, forming thermally stable Al$_x$O$_y$ clusters. (2) The Al$_x$O$_y$ clusters effectively act as a catalyst support and promote the formation of Fe catalyst nanoparticles. We envision that the relationship between nanoparticle formation and the role of Al$_x$O$_y$ in the Fe/Al system is similar to that in the Ni/Al system reported by Zhang et al [11].

Figure 3(a) shows a typical SEM image of CNTs synthesized directly on a Ta substrate by thermal CVD using an Fe/Al multilayer catalyst. The CNTs approximately 80 μm in length grow perpendicular to the substrate surface. From a magnified image (Fig. 3(b)), the CNTs are found to have a high density of $10^{10}$ cm$^{-2}$. Figure 3(c) shows an EDLC single-cell test device fabricated using the grown CNTs as electrodes. Two CNT electrodes were separated by the cellulose separator. The device was immersed in 1 M tetraethylammonium tetrafluoroborate (TEABF$_4$) / propylene carbonate (PC) electrolyte.

From the charge/dischage cycle characteristics, the specific capacitance of the test cell was estimated to be 10.7 F/g. The specific capacitance was found not to deteriorate even after 5,000 cycles, indicating a stable charge/dischage cycle characteristic. The specific capacitance of vertically aligned CNTs with a long length and a high density was also found to be approximately 36 times that of randomly oriented CNTs with a short length of 6-8 μm [4]. However, the specific capacitance obtained here is not sufficiently high for application to energy storage devices. Thus, an improvement in the wettability of the CNT electrodes in the electrolyte might be necessary to increase specific capacitance.

B. Towards Highly Efficient Field Electron Emitter

Electron field emission from nanostructure materials such as CNTs is a wide and interesting subject of research in science and technology, and is related to the fabrication of field-emission displays. Related studies have focused on exploring highly efficient field-emitting materials and their nanotechnology [12–17]. Although the field emitters reported to date require a threshold electric field ($E_{th}$) of 2~3 V/μm at minimum to produce a technologically useful current density of 10 mA/cm$^2$ [18–24], it is important to lower the $E_{th}$ to achieve practically applicable field electron emitters that operate with a low power consumption. Regarding an aligned CNT array as a field emitter, it has been predicted that field emission becomes maximum when the ratio of intertube distance to the height of each individual CNT is approximately 2 [25]. To date, however, this ideal arrangement of CNTs for electron field emission has not yet been realized.

In this section, we describe the fabrication of an architecture that satisfies optimal conditions using pillars of aligned CNT bundles [26], which are grown using the method for the synthesis of long and high-density CNTs described before.

Figure 4 shows the fabrication procedure for a pillar array of aligned CNT bundles. First, the Si substrate was spin-coated with 1.8 μm of photoresist (Shipley Company, Microposit S1813) and baked at 80°C for 30 min (Fig. 4(a)). The resist was developed at room temperature, forming a patterned resist (Fig. 4(b)). Then, an Fe/Al multilayer thin film was deposited on the substrate by magnetron sputtering (Fig. 4(c)). Lift-off was carried out by ultrasonic agitation in acetone, resulting in the formation of a patterned Fe/Al multilayer thin film (Fig. 4(d)). Finally, to grow a pillar array of aligned CNT bundles, thermal CVD was performed at 700°C for this sample in the conditions as listed in Table 1 (Fig. 4(e)).

Figure 5(a) shows an SEM image of the pillar of aligned
FIG. 3: (a) Cross-sectional SEM image of long and high-density CNTs. (b) Enlarged image of Fig. 3(a). (c) Schematic diagram of the EDLC test cell using long and high-density CNTs as electrodes.

FIG. 4: Schematic diagram of fabrication procedure for synthesis of pillar array of aligned CNT bundles.

CNT bundles grown on a Si substrate. The pillar with a diameter of 50 µm is aligned perpendicular to the substrate surface. From Fig. 5(b), the pillar was found to be composed of CNTs with a number density of approximately $10^{10}$ cm$^{-2}$. The TEM observation of CNTs (Fig. 5(c)) revealed the formation of multiwalled CNTs (MWNTs) with a diameter of approximately 9 nm.

To obtain an optimal R/H of 2, a pillar height (H) of approximately 125 µm and an interpillar distance (R) of 250 µm were adopted. Figure 6 shows an SEM image of the optimized pillar array of aligned CNT bundles grown on the Si substrate. The number density of the pillar is $1.6 \times 10^3$ cm$^{-2}$.

We have observed the field electron emission of the technologically useful current density of 10 mA/cm$^2$ at an extremely low $E_{th}$ of 1.0 V/µm, from the pillar array fabricated at an optimal R/H of 2. Figure 7(a) shows the current density vs electric field characteristics ($J - E$ plot) of the pillar array. The applied electric fields at the emission current densities of 10 µA/cm$^2$ and 10 mA/cm$^2$ are defined as turn-on field and $E_{th}$. The turn-on field and $E_{th}$ were 0.4 V/µm and 1.0 V/µm, respectively. The Fowler-Nordheim (FN) plot shown in the inset of Fig. 7(b) verifies the current results from the electron field emission. As shown in Fig. 7(c), the fluctuation of the field emission of a current density of 1 mA/cm$^2$ is within 5% for a 30 h test. Moreover, the electron field emission was monitored by a fluorescent screen at an electric field of 0.9 V/µm, as shown in the inset in Fig. 7(c). The emission uniformity and high brightness are clearly evident. These results indicate that the practical requirements for field-emission devices are satisfied.

The highly efficient field emission readily achieved by the simple architecture of the pillar array of aligned CNT
FIG. 5: (a) SEM image of pillar of aligned CNT bundles grown by thermal CVD. (b) Enlarged SEM image of the pillar. (c) TEM image of the aligned CNT. The inset in (c) shows the electron diffraction pattern of the CNT.

FIG. 6: SEM image of pillar array of aligned CNT bundles.

bundles is attributed to the optimal R/H. From the FN plot, the apparent field enhancement factor ($\beta$) of the FN equation was estimated to be approximately 14000 by setting the work function to be 5 eV. We envision that the reason such a high $\beta$ was obtained even for the 50-\mu m-diameter pillar is that the CNTs on the periphery of the pillar induce a dominant electrical field concentration on their tops, acting as major emission sites. When R/H is not optimized or the film is not patterned, a higher $E_{th}$ and a lower $\beta$ were obtained with the same height of H.

The threshold electric fields, $E_{th}$, for various carbon-related materials such as CNTs [18, 19], nanohorns [20], carbon fibers [21], nanostructured carbon [22], and diamond [23], as well as that for Mo tips [24] and Si tips [24] have been reported. The $E_{th}$ obtained in this study is 1/2-1/3 times lower than the lowest values that have been reported for any field-emitting materials. Thus, the field electron emitter presented here can facilitate lowering of the power consumption in field-emission displays, light sources with high brightness and so on.

For the practical fabrication process of a field-emission display, the low-temperature synthesis of CNTs is indispensable. Plasma-enhanced CVD is one of the most promising methods for low-temperature synthesis. As shown in Fig. 8, we have already succeeded in synthesizing aligned carbon nanofibers at 200°C by plasma-enhanced CVD [27].

III. COMPOSITES OF CARBON NANOTUBES AND INORGANIC MATERIALS

A. Coating Technique of Carbon Nanotubes

Nanostructured hybrids between CNTs and other materials are indispensable for the application to CNT-based nanodevices. For example, field-effect transistors (FETs) [28], single-electron transistors (SETs) [29], and gas sensors [30] have been fabricated using the combination of an insulator with a CNT. It has been shown that the electronic properties of these nanodevices are easily affected by the molecular species adsorbed on the surface and interface of CNTs [31, 32]. In this aspect, the method of coating CNTs with inorganic materials in multishell form is one of the most desirable approaches to fabricating CNT composites that act as building blocks. Although other types of multishell nanowires/nanotubes have been reported thus far [33-35], for the synthesis of insulator-coated CNTs, two typical methods have been studied. One is a sol-gel method using tetraethoxysilane (TEOS) [36]. The other is atomic-layer deposition using trimethylaluminum (TMA) [37]. However, to date, a method for precise control of the thickness and stoichiometry of insulator-coated CNTs has not been established.

In this section, we describe a method of synthesizing...
thin layer-coated CNTs by pulsed laser deposition (PLD), in which the thickness of the thin coated layer can be controlled to nanometer-scale accuracy [38]. We also demonstrate local etching of the thin layer-coated CNTs by reactive ion etching (RIE) [39].

Figure 9(a) shows the PLD apparatus used for coating CNTs with a thin layer. The base pressure of the chamber was $1 \times 10^{-5}$ Pa. A pulsed Nd:YAG laser with a wavelength of 355 nm and a pulse duration of 5 ns was focused onto a target at a repetition rate of 10 Hz. The laser energy was fixed at 140 mJ. A specimen was set at the tip of the specimen holder, and was placed 40 mm from the target. The angle $\alpha$ between the axis of the holder (the CNT axis) and the normal direction of the target was $45^\circ$. The azimuth angle $\varphi$ of the specimen was changed during PLD. As shown in Fig. 9(b), the specimen was prepared using a Mo plate (3 mm diameter) with an isolated CNT attached by electrophoresis [40]. We used multiwalled CNTs (MWNTs) with an average diameter of 20 nm and a length of over 2 $\mu$m, which were synthesized by the arc discharge method. In this experimental configuration, the coating of CNTs with SiO$_2$ was carried out at room temperature using a single-crystal Si target ($15 \times 15$ mm$^2$) under a pressure of $1 \times 10^{-2}$ Pa maintained by flowing oxygen gas. The deposition time of SiO$_2$ varied from 5 to 120 min.

Figure 10(a) shows a TEM image of the product synthesized by 30 min of PLD. An SiO$_x$ layer was found to be uniformly coated on the MWNT with a thickness of approximately 8 nm. Figure 10(b) shows a selected-area electron diffraction pattern of the SiO$_x$-coated MWNT. Graphite (002) and (004) spots were clearly observed, indicating that the inner MWNT has a good crystallinity. A diffraction pattern originating from SiO$_2$ was not observed, showing that the coated SiO$_x$ layer was amorphous. Figure 10(c) shows an EDX spectrum from the center of the SiO$_x$-coated MWNT. Peaks originating from C, O, and Si were dominantly observed. The Mo peak originates from the Mo plate of the specimen. From the peak intensities, the composition ratio of O to Si, $x$, was estimated to be $2.4 \pm 0.1$. Thus, the product was found to have a nearly stoichiometric SiO$_2$ layer.

Figure 11 shows a high-resolution TEM image of the tip of the MWNT coated with an SiO$_2$ thin layer formed by 5-min PLD. The top of the MWNT had a triangular shape. The thickness of the SiO$_2$ layer was approximately 2 nm. As we can see, the SiO$_2$-coated CNT maintained the shape of the inner MWNT. At sidewall regions A and B, uniform SiO$_2$ thin layers were observed. Even along the slope of the tip, region C, an SiO$_2$ thin layer with a uniform thickness was formed on the MWNT. Thus, an ultrathin SiO$_2$ layer of approximately 2 nm was uniformly wrapped around the MWNT, reflecting the shape of the MWNT.

Figure 12 shows the dependence of deposition time on the thickness of the SiO$_2$ coating layer. The TEM images in Figs. 12(a), 12(b), and 12(c) correspond to 5, 30, and 60 min depositions, respectively. As seen in Fig. 12(d), thickness is proportional to deposition time, showing that the deposition rate in PLD is constant (approximately 0.3 nm/min). We confirmed that even for 120 min of PLD, a uniform SiO$_2$ layer was wrapped around the MWNT. Thus, we successfully performed precise thickness control.
FIG. 9: (a) Schematic illustration of a pulsed laser deposition apparatus. (b) SEM image of an isolated-MWNT specimen for thin layer coating.

FIG. 10: (a) TEM image, (b) selected-area electron diffraction pattern, and (c) EDX spectrum of the SiO$_2$-coated MWNT synthesized by 30 min of PLD.

of the stoichiometric SiO$_2$ layer wrapped around CNTs with nanometer-scale accuracy. This originates from the advantages of PLD that enable the control of the growth rate and composition [41].

We show the geometric effect on the coating of CNTs with an SiO$_2$ layer. Figures 13(a) and 13(b) show the TEM images of SiO$_2$-coated CNTs at the $\alpha$ of 0° and 45°, respectively. The schematic diagrams of the geometry between the CNTs and the target during PLD are shown in the insets of the Figs. 13(a) and 13(b). Note that the azimuth angle $\phi$ of the specimen was fixed during PLD. In Fig. 13(a), the SiO$_2$ layer was concentrated at the top of CNTs. On the other hand, in Fig. 13(b), only one side of the CNT walls was coated with an SiO$_2$ layer. Thus, the geometry of PLD shown in Fig. 9(a) is an essential factor in achieving a uniform coating.

Next, we demonstrate a method for the local etching of insulator-coated CNTs by RIE with high controllability of the exposed tip length [39]. Figure 14 shows the experimental procedure for fabricating passivated nanoprobe structures. First, CNTs perpendicular to the sample surface (V-CNTs) were synthesized using rf magnetron sputtering (Fig. 14(a)) [42, 43]. Ten-nanometer-thick Ni thin films deposited on the n-Si(100) wafer with a resistivity
of 3.5 Ω·cm were used as substrates. The catalytic Ni nanoparticles were prepared by dipping the substrate into a 2.5% HF solution for 8 min and subsequent annealing at 700°C for 1 h. In the growth of V-CNTs by sputtering, N₂ gas was introduced into the chamber at a pressure of 2.7 Pa, and a plasma was generated at an rf power of 100 W at 700°C for 8 h. The diameter, length and number density of the resultant V-CNTs were approximately 70 nm, 1.4 µm, and 9 × 10⁸ /cm², respectively. Second, the V-CNTs were coated with 20-nm-thick SiO₂ thin layers by PLD (Fig. 14(b)). The coating of the V-CNTs with SiO₂ was carried out at room temperature using a single-crystal Si target under a pressure of 1.3 × 10⁻² Pa maintained by flowing O₂ gas for 3 h. Experimental details on the PLD were described previously. Third, the substrates were spin-coated with a 1.8-µm-thick photore sist (Shipley Company, Microposit S1813) and baked at 80°C for 30 min (Fig. 14(c)). Fourth, the local etching of the SiO₂ layer at the tip was carried out by RIE (Fig. 14(d)). The substrates were placed in an RIE chamber and etched in a CF₄ plasma (15 sccm) for 0 to 30 min at room temperature. This process was conducted at a gas pressure of 4.7 Pa and a power density of 0.20 W/cm². Finally, the photoresist was stripped from the substrate by ultrasonic agitation in acetone for 10 min (Fig. 14(e)).

Figures 15(a)-15(c) show SEM images of the resultant products as functions of etching times of 0, 10 and 30 min, respectively. By the RIE, the SiO₂ layer at the tip of the SiO₂-coated CNTs was found to be clearly removed. The light gray triangle at the tip in Fig. 15(c) indicates a Ni catalyst nanoparticle [43], showing that the CNT remained without crucial damage. For 10 min and 30 min etchings, the average lengths of the exposed CNTs were 80 nm and 385 nm, respectively. It was found that the length is proportional to etching time. The etching rate was estimated to be 16 nm/min. Thus, when the V-CNT length and the thickness of the photoresist are given, the etching length can be precisely controlled via the etching time with nanometer accuracy. We investigated the ef-
FIG. 13: Geometric effect on coating CNT with thin layer. (a) and (b) are TEM images of CNTs coated with SiO$_2$ layer at $\alpha=0^\circ$ and $\alpha=45^\circ$, respectively. The insets in (a) and (b) show schematic diagrams of geometry between the CNTs and the target during PLD.

FIG. 14: Schematic diagrams of experimental procedure for local etching of insulator-coated CNTs.

fect of the RIE process on the crystallinity of the exposed CNT. The high-resolution TEM observation showed clear graphite lattices at the topmost wall of the CNT as well as on the inside after the etching for 30 min. This suggests the destruction of the graphite layer of the CNT by plasma species such as CF$_2^+$ and F$^*$ rarely occurs at up to 30 min of etching time. Prolonged etching over 30 min could degrade the crystallinity of the CNT.

B. Nanoprobe Application

In the use of CNT tips in scanning probe microscopy (SPM), their high aspect ratio and small effective radius offer the possibility of probing deep grooves at a high lateral resolution [44] exceeding those achieved using the conventionally used Si tips in atomic force microscopy (AFM). Another feature of the CNT tip is its mechanical flexibility which can reduce damage to delicate organic and biological molecules [45, 46]. The CNT tip can also be utilized for scanning tunneling microscopy/spectroscopy (STM/STS). To date, the STM imaging of TaS$_2$[44], Si(111)-7 $\times$ 7 [47] and Au(111) [48] surfaces has been reported. However, with respect to probing the surface electronic state, a CNT tip for STM/STS observation has not been fully established due to the following factors. The high contact resistance between the supporting tip and the attached CNT strongly disturbs electron transport in the tip. Moreover, adsorbates contained in the CNT degrade the surface cleanliness of the specimen under STM operation [47]. These factors cause difficulties in stable atomic imaging and spectroscopy. Considering this, the
metal coating of the CNT tip ensemble is likely to be the most promising practical method of STM/STS.

In this section, we describe the development of a metal-coated CNT tip for STM/STS using the PLD described before. The observation of a Si(111)-7 × 7 surface using the W-coated CNT tip demonstrated stable atomic imaging and the potentiality of STS measurement, which can be achieved from the pristine stage without any pretreatments of the tip [49].

The W-coated CNT tip was fabricated by the following procedure. First, a CNT was attached to a W tip in a field-emission scanning SEM chamber equipped with tip and sample stages, which can be independently manipulated by piezoactuators. An electrochemically etched W tip and MWNTs aligned on a Mo plate by electrophoresis were set on the former and latter stages, respectively. We used MWNTs produced by the arc discharge method, which were 20 nm in diameter and over 3 μm in length. The W tip was moved to contact the MWNT, and then adhesion between them was achieved by irradiating the contact area with an electron beam [50]. Second, the CNT tip was coated with a W thin layer by the PLD method. The coating of the CNT tip with W was carried out at room temperature using a W target (purity; 99.9%) under a pressure of 1 × 10−5 Pa. The deposition time of W was varied from 30 to 60 min. The W-coated CNT tip thus fabricated was introduced into an ultrahigh vacuum (UHV)-STM system. The phosphor-doped Si(111) wafer was used as the specimen. The clean Si(111)-7 × 7 reconstructed surface was prepared by conventional thermal flashing in UHV. No pretreatments of the tip such as thermal flashing or prolonged annealing were carried out.

Figure 16(a) shows a TEM image of the W-coated CNT synthesized by 30 min of PLD. A W layer was found to be uniformly coated on the MWNT, reflecting the shape of the inner MWNT [38]. Figure 16(b) shows a magnified image of the interface region in Fig. 16(a). The W layer has a thickness of approximately 3 nm and the fringes of graphite layers were clearly observed, indicating that the crystallinity of the inner MWNT was maintained. Figure 16(c) shows a typical SEM image of the W-coated CNT tip. The thickness of the W layer was approximately 6 nm. The curvature of the W tip apex was approximately 100 nm, and the length and diameter of the attached CNT were approximately 150 nm and 32 nm, respectively.

STM observation was performed using the W-coated CNT tip. Figures 17(a) and 17(b) show STM images of empty and filled states on the Si(111)-7 × 7 surface, at a sample bias voltage of ±1.55 V and a tunneling current of 0.4 nA. The atomic images of both states were clearly observed. In particular, the difference between the faulted and unfaulted halves in the dimer-adatom-stacking fault (DAS) structure was recognized in the filled state. These images could be observed stably for a period of over 1 h. Moreover, the same results were obtained using other W-coated CNT tips fabricated separately, indicating the high reproducibility of our method. Figure 17(c) shows STS spectra for the rest atom (A), corner adatom (B), and center adatom (C), whose positions are indicated by the magnified atomic STM image (Figure 17(d)). Although the tendency of the spectra does not strictly coincide with reported ones [51–54], each spectrum exhibits a different feature; it can be inferred that a peak at 0.8 eV for the rest atom is due to the dangling bond state, while shoulders at −0.3 eV for the corner and center adatoms originate from their adatom state. For the center adatom, a peak at +0.5 eV was markedly observed compared with that for the corner adatom. It is stressed that this is the first demonstration of such a site-dependent STS measurement using a CNT tip. After STM/STS observation, we con-
FIG. 17: (a) and (b) show atomic STM images of Si(111)-7 × 7 for empty and filled states, respectively, obtained using the W-coated CNT tip. ($V_s = \pm 1.55$ V, $I_t = 0.4$ nA, 15 nm ×15 nm). (c) Site-dependent STS spectra obtained at the rest atom (curve A), corner adatom (curve B), and center adatom (curve C) on the Si(111)-7 × 7 surface. (d) Enlarged atomic STM image of Si(111)-7 × 7 for empty state.

confirmed that the W-coated CNT existed at the tip, from the SEM observation.

We also demonstrated the mechanical robustness and flexibility of the W-coated CNT tip. Figure 18 shows a series of SEM images of the W-coated CNT tip measured by changing the distance between the tip and a Mo plate, d. We used a 2-µm-long CNT coated with a 3-nm-thick W layer. Arrows in this figure indicate the direction of the tip movement. Upon contact with the plate, the tip began to bend gradually as d was shortened. When the tip was retracted from the contact point, it was restored to its initial shape. Pristine CNT tips, which were not coated with a W layer, showed similar behavior. Thus, we found that the W-coated CNT tip has mechanical robustness and flexibility even though the tip was coated with a metal layer. In other words, the mechanical properties of the tip were maintained by virtue of the thin coated layer with nanometer-order thickness.

We envisioned that the atom-resolved imaging and spectroscopy achieved by the W-coated CNT tip stems from a low contact resistance between the W tip and the CNT, and passivation of the entire region of the tip by W coating. The metal coating of a CNT tip as a template provides a W nanowire tip for STM, on which the nanoscale protrusion necessary for interatomic electron tunneling is formed from the outset. This enables stable atomic imaging from the pristine stage. Our method has a practical advantage in that STM operation can be
FIG. 18: Series of SEM images of the W-coated CNTs measured with varying the distance, \( d \), between the tip and a Mo plate.

FIG. 19: Applications of an insulator-coated CNT to nanodevices.

performed without any pretreatment of the tip such as prolonged thermal annealing.

IV. CONCLUSION

In this review, we demonstrate the device-oriented synthesis of CNTs, by taking an EDLC and a field electron emitter as examples. As one of the most desirable approaches to fabricating nanostructured hybrids between CNTs and inorganic materials, we present a method of coating CNTs with inorganic materials in multishell form, and its application for STM/STS tips. The CNT coated with an insulator having well-controlled thickness has a high potential for versatile applications to CNT-based nanodevices. For example, the insulator-coated CNT itself can be utilized as a building block of a coaxially gated FET (Fig. 19(a)) which has been theoretically predicted to exhibit significantly good performance [55]. For CNT nanoprobes including sensors [56], chemical detectors [57] (Fig. 19(b)), and tools for measuring electronic signal transmission between living cells (Fig. 19(c)), insulation and passivation of the CNT are indispensable when they are used in a biochemical environment. Moreover, the CNT tip coated with a metal having well-controlled thickness offers the potential of versatility in its application as a conducting nanoprobe. For example, utilizing its mechanical robustness and flexibility, the probe presented here can be applied to electron transport measurements on the nanoscale by multiprobe STM [58]. Thus, our coating method for CNTs can facilitate the fabrication of the building blocks of CNT-based nanodevices.

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