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Citation: *Applied Physics Letters* **90**, 263104 (2007); doi: 10.1063/1.2745226

View online: <http://dx.doi.org/10.1063/1.2745226>

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# ZnO nanoparticle growth on single-walled carbon nanotubes by atomic layer deposition and a consequent lifetime elongation of nanotube field emission

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(Received 9 January 2007; accepted 9 May 2007; published online 25 June 2007)

ZnO nanoparticles were grown on single-walled carbon nanotubes (SWNTs) by atomic layer deposition using diethylzinc (DEZ) and water. The authors discuss that, because of chemical inertness of nanotubes to DEZ and water molecules, such nanoparticles are not likely to grow on the wall of clean and perfect nanotubes. Rather, the growth of ZnO nanoparticles should be attributed to imperfection of nanotubes, such as defects and carbonaceous impurities. Lifetime of field emission from SWNTs with the ZnO nanoparticles is 2.5 times longer than that from the as-grown nanotubes. It is thought that the protection of the defects or impurities by ZnO nanoparticles mainly contributed to the improvement of the field emission lifetime from SWNTs. © 2007 American Institute of Physics. [DOI: 10.1063/1.2745226]

Owing to the inherent geometrical advantages, namely, the one dimensional shape with nanoscale diameters, immense research works have been devoted to utilizing nanotubes as cold cathodes, for example, of field emission displays (FEDs), lightning elements, and discharge tubes.<sup>1,2</sup> In particular, single-walled carbon nanotubes (SWNTs), in comparison with multiwalled nanotubes (MWNTs), have been demonstrated to produce a larger emission current with a lower turn-on field ( $E_{to}$ ) and a lower threshold field ( $E_{th}$ ).<sup>3</sup> These superiorities of the SWNTs have been attributed to their atomically sharp shape, high electrical conductivity, and large aspect ratio ( $>10^3$ ).<sup>1,2</sup> However, an immediate concern over the SWNT electron emitters is the stability against a long time operation.<sup>4</sup> The poor stability of SWNTs may be due to destruction of nanotube structure primarily through ion bombardments during field emission. The ion bombardments are certainly more harmful to the SWNTs with imperfections or impurities.<sup>4</sup>

In this regard we conjectured that a selective growth of protecting materials on the defective sites may lead to a lifetime improvement of the field emission from SWNTs. In order to retain the advantageous emission properties of the SWNTs, the protecting material should cover only the defective region, rather than coating the whole SWNTs. In addition, it could be more advantageous for the protecting materials to be conducting, to avoid a degradation of emission current due to the presence of nonconducting materials on the cathode surface.

Atomic layer deposition (ALD) method is a special modification of chemical vapor deposition for self-limiting

growth of thin films.<sup>5</sup> In ALD method, thin films are grown by surface reactions between precursors and surface functional groups. Therefore if there are no reactive sites or functional groups on the surface for the ALD reaction to occur, thin film cannot be grown by this method. The clean nanotube surface is known to be quite inert so that the conformal deposition of thin films by ALD method has been very rare. It is noteworthy that the conformal coating of thin films on SWNTs was realized only after the covalent or noncovalent functionalization of nanotube wall.<sup>6,7</sup> Thus it is highly probable that the ALD method could lead to the selective growth of a protective material only on the defective sites of SWNTs.

In this work, ZnO nanoparticles were grown by ALD to protect the nanotube electron emitters. ZnO is a well-known *n*-type semiconductor with a direct wide band gap (3.3 eV at 300 K).<sup>8</sup> Furthermore, it has been demonstrated that the atomic-layer-deposited ZnO films are generally conducting with a low resistivity in the order of  $10^{-2}$ – $10^{-3}$   $\Omega$  cm,<sup>9</sup> thereby satisfying aforementioned requirements for the protecting material. Recently, Green *et al.* reported that ZnO-coated MWNTs showed enhanced electron emission properties.<sup>10</sup> They obtained ZnO films on the wall of MWNTs by ALD, and the bead-shaped ZnO particles were formed by a subsequent annealing at 900 °C. However, such a high temperature annealing is not preferred for the optoelectronic applications such as FEDs.

Here, we show that the ALD using diethylzinc (DEZ) and water leads to the direct formation of the ZnO nanoparticles on the wall of SWNTs *without any annealing*. We discuss that the nonconformal growth of ZnO nanoparticles are attributed to the presence of defects and/or impurities of nanotubes. It was also demonstrated that the SWNTs coated with ZnO nanoparticles have longer lifetime of field emis-

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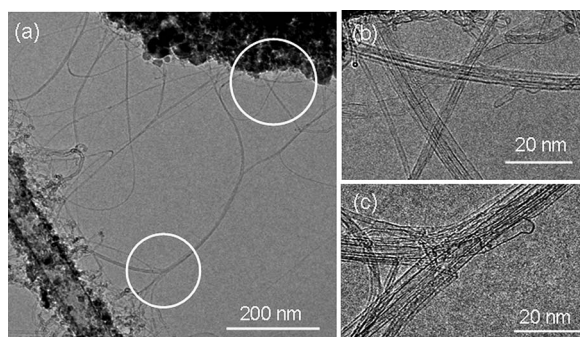


FIG. 1. TEM images of suspended nanotubes directly grown on a TEM grid. (a) Low resolution image. [(b) and (c)] Magnified high resolution images from the areas indicated by circles in (a).

sion, compared to that of the as-grown nanotube.

To investigate the growth behavior of ZnO purely on the wall of nanotubes, we prepared suspended nanotubes, which are necessary to avoid the surface-assisted growth from the substrate to the nanotube wall during the ALD process. The suspended nanotubes were directly grown on transmission electron microscopic (TEM) grids. Nanotube growth was performed with the same condition, as described elsewhere.<sup>11</sup> Figure 1 shows the suspended nanotubes directly grown on TEM grids. As shown in the high-resolution magnified images in Figs. 1(b) and 1(c), the suspended nanotubes are single walled. Some of them are individually separated but the majority of them are bundled.

ALD of ZnO was performed on the grid specimen with suspended nanotubes at 200 °C using DEZ and water.<sup>9</sup> Figure 2 shows that nanoparticles grow on the wall of nanotubes. In later paragraph we will discuss that the ALD is not likely to lead to formations of nanoparticles on the wall of perfect nanotubes. However, it is practically impossible to obtain perfect nanotubes without defects and impurities. It is believed that the nanoparticle growth was initiated on the

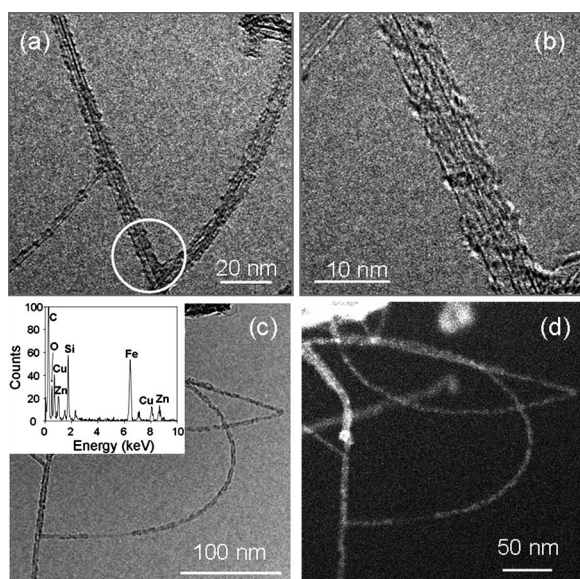


FIG. 2. ZnO nanoparticles grown on the wall of suspended nanotubes. (a) TEM image of ZnO nanoparticles grown for 37 cycles. (b) Magnified high resolution image from the areas denoted by the circle in (a). (c) TEM image of ZnO nanoparticles grown for 200 cycles. (d) Z-contrast image of the same area in (c). The inset shows an EDS spectrum of the sample used for Fig. 2(c).

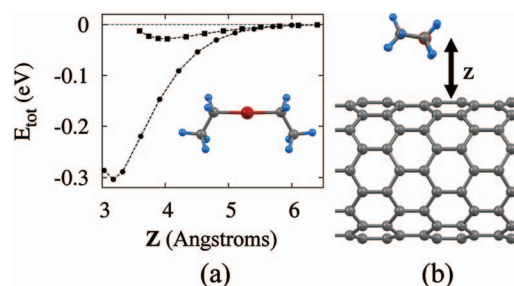


FIG. 3. (Color) (a) Potential energy curves and (b) atomic geometry for the DEZ molecule adsorbed on the (10,0) nanotube. Squares and circles in (a) are the calculation results with LDA and GGA, respectively. Perspective view of the DEZ molecule is shown in the inset of (a). The red, gray, and blue spheres represent zinc, carbon, and hydrogen atoms, respectively.  $Z$  is the distance between the DEZ molecule and the nanotube surface.

defective sites or impurities in a nonconformal manner by ALD. The nanoparticles grown for 37 cycles are randomly distributed on the wall of nanotubes, and the size of the nanoparticles is smaller than 3 nm, as shown in Figs. 2(a) and 2(b). The nanoparticles are amorphous in Fig. 2(b). The nanoparticle-free regions in the wall of nanotubes are clearly resolved without any films in Fig. 2(b).

If the nanoparticle growth could occur on the defect- or impurity-free region of the nanotube wall, a further repetition of ALD cycles should have resulted in a film-shaped ZnO layer covering the nanotubes. However, the deposited ZnO remained still in the form of nanoparticles even after 200 cycles [Fig. 2(c)]. The size of ZnO particles is smaller than 5 nm. The Z-contrast TEM image in Fig. 2(d) clearly shows the grown ZnO nanoparticles, where the bright particles are ZnO and the dark lines are nanotubes. To further confirm the chemical composition of the nanoparticles, TEM-energy dispersive spectroscopic (EDS) spectrum is shown in the inset of Fig. 2(c). The strong carbon signal and weak Zn and O signals support that the grown nanoparticles are ZnO. The other signals of Cu, Fe, and Si are contributed by the grid, catalyst, and Si(Li) window of the EDS detector, respectively. Therefore it is believed that the nanoparticles are formed only on the defective sites or impurities on the wall of nanotubes, which are likely to provide strong chemisorption sites for DEZ molecules or water.

We investigate the adsorption energetics of DEZ on the clean and perfect wall of a (10,0) nanotube using the first-principles electronic structure calculation. For computation, we use the density functional method,<sup>12</sup> adopting the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange-correlation potential.<sup>13</sup> The ionic pseudopotentials are described via the projector augmented wave, and the cutoff energy for the plane-wave basis is set to 500 eV.<sup>14</sup> To investigate the adsorption energetics we calculate the total energy of the DEZ-adsorbed nanotube system, while rigidly shifting the DEZ molecule to the positions with selected distances from the nanotube. As shown in Fig. 3, the adsorption energy with LDA calculation (0.30 eV) is much higher than that with GGA calculation (0.03 eV). The equilibrium distance between DEZ and nanotube is found to be 0.32 and 0.38 nm in the LDA and GGA calculations, respectively.

While the density-functional description for weak intermolecular interactions may not be quantitatively correct, the real physical situation is likely to be in between the LDA and GGA results.<sup>15,16</sup> The small binding energy as well as the

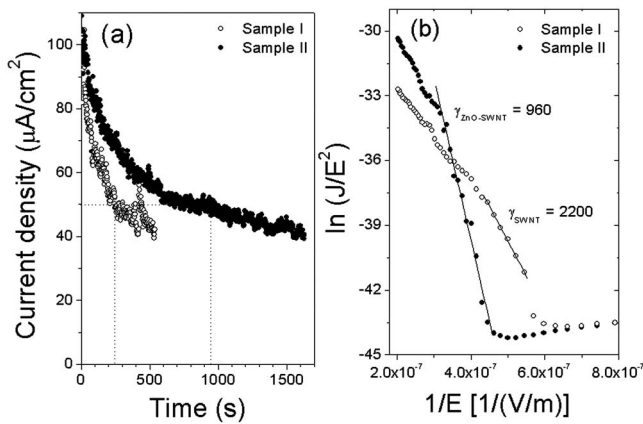


FIG. 4. (a) Emission current variations with time for lifetime measurements. (b) Fowler-Nordheim plots. Sample I has SWNTs without ZnO nanoparticles and sample II has SWNTs with ZnO nanoparticles grown by ALD.

long binding distance obviously show that the adsorption of DEZ molecule on the clean nanotube wall is a mere physisorption. As well known, water molecules also physically adsorb on the wall of nanotubes.<sup>17</sup> Generally, the physisorbed molecules have very short residence time, whose half-lives are in the order of  $\sim 10^{-8}$  s at room temperature.<sup>18</sup> Therefore, considering the ALD temperature (normally 150–300 °C) and the long purging time over 1 s with inert gas, the growth of ZnO on clean and perfect nanotubes cannot be initiated by the ALD process using DEZ and water.

We now compare the field emission properties of the as-grown (sample I) and the ZnO nanoparticle-coated (sample II) nanotubes in Fig. 4. The experimental details are previously reported.<sup>9,11</sup> For sample II, after SWNT growth, ALD of ZnO was performed at 250 °C for 70 cycles in order to form ZnO nanoparticles. Figure 4(a) shows the emission current variation with measurement time of the two samples. Half-lives of the emission current where it decays from 0.1 to 0.05 mA/cm<sup>2</sup> are 250 and 950 s, respectively. The lifetime of emission current was elongated by around 2.5 times by the formation of ZnO nanoparticles. This result supports that the ZnO nanoparticles are formed on defective sites or impurities, which otherwise were responsible for the poor lifetime in the electron emission from SWNTs.

Field emission is typically analyzed with the Fowler-Nordheim (FN) model, which describes the tunneling of electrons through a metal-vacuum potential barrier. Samples I and II show a FN tunneling behavior in the electric field ranging from  $\sim 1.8 \times 10^6$  to  $2.2 \times 10^6$  and  $\sim 2.3 \times 10^6$  to  $3.1 \times 10^6$  V/m, respectively. The deviation from the FN behavior at higher fields might be originated from the degradation of the emitters. To maximize the emission current for a given applied voltage, the emitter should have a low work function and should be shaped as sharp as possible to offer the highest field enhancement factor ( $\gamma = F/E$ , where  $F$  is the local field at the emitter tip and  $E$  is the macroscopic field). Figure 4(b) shows FN plots of the two samples. Assuming that work functions of the nanotube tips are 4.8 eV,<sup>9</sup> the field enhancement factor ( $\gamma_{II} \sim 960$ ) of sample II, which can be calculated

from the slope of the FN plot,<sup>9,11</sup> is smaller than that ( $\gamma_I \sim 2200$ ) of sample I. The lower field enhancement factor of sample II is possibly due to the larger effective diameter of the ZnO-nanoparticle-coated nanotubes than that of the uncoated SWNTs. The enhanced electron emission properties of the ZnO-coated MWNTs by Green *et al.*<sup>10</sup> were attributed to the additional emission from polyhedral nanoparticles with large diameters (10–30 nm). On the other hand, our nanoparticles have much smaller diameter ( $< 3$  nm) with spherical shape of which the additional emission is negligible. The threshold field strength of sample II for the linear FN behavior ( $2.3 \times 10^6$  V/m) is higher than that of sample I ( $1.8 \times 10^6$  V/m), which may be due to a larger effective diameter of sample II. The FN plot for sample II remains linear up to  $(3.1 \times 10^6$  V/m) while that of sample I deviates from the linear behavior at  $(2.2 \times 10^6$  V/m). This also confirms that sample II is more durable against degradation.

In summary, ZnO nanoparticles were grown on SWNTs by ALD using DEZ and water. Because the clean and perfect nanotubes are chemically inert, the ZnO nanoparticles are not likely to be grown on them. Therefore, the observed ZnO nanoparticles after the ALD cycles were attributed to the existence of defect sites or impurities on the wall of nanotubes. It was shown that the lifetime of field emission from SWNTs was improved by  $\sim 2.5$  times after growing the ZnO nanoparticles, due to the protection of the defects or impurities on the wall of nanotubes.

This work was supported by the Tera-Level Nano-Devices (TND) Program of the Ministry of Science and Technology, Korea.

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