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Article first published online: 26 JUN 2012

DOI: 10.1002/pssa.201228171



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**Keywords:**
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## Abstract

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We describe a new method for the manufacture of single-walled carbon nanotube (SWCNT)-based electrical devices on flexible substrates. The method involves the deposition of a SWCNT films onto polydimethylsiloxane (PDMS) substrates from rigid substrates using the adhesive property of PDMS. This method is similar to the conventional dry transfer method, which is based on surface-energy modification, except that our method involves mechanical transfer using the adhesive property of PDMS under peculiar

Phys. Status Solidi A **209,** No. 10, 2082–2086 (2012) / **DOI** 10.1002/pssa.201228171

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# Carbon-nanotube-based flexible devices using a mechanical transfer method

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Received 7 March 2012, revised 15 May 2012, accepted 25 May 2012
Published online 28 June 2012

**Keywords** carbon nanotubes, field-emission displays, flexible sensors, gas sensors

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We describe a new method for the manufacture of single-walled carbon nanotube (SWCNT)-based electrical devices on flexible substrates. The method involves the deposition of a SWCNT films onto polydimethylsiloxane (PDMS) substrates from rigid substrates using the adhesive property of PDMS. This method is similar to the conventional dry transfer method, which is based on surface-energy modification, except that our method involves mechanical transfer using the adhesive property of PDMS under peculiar conditions. The gas-sensing characteristics of the resulting transferred SWCNT films are presented, showing, for example, that typical flexible sensors exhibit a sensitivity of 17.4% for 4-ppm $NO_2$ in a vacuum at room temperature. The performances of the devices are slightly reduced when they are bent to a curved profile with a bending radius of 2 cm (15.9%). The field-emission properties are also investigated. From these emitters, the SWCNTs can be turned on with a field as low as 0.9 V/μm, and an emission current density of 0.75 mA/cm$^2$ at 1.2 V/μm can be attained. Thus, a method for the fabrication of flexible devices is established, which should find practical applications in electronic devices.



**1 Introduction** Single-walled carbon nanotubes (SWCNTs) have great potential for use in electronic devices because of their exceptional electrical, mechanical, and electromechanical properties. The electrical properties of SWCNTs are a strong function of their atomic structure and mechanical deformations, and such relationships make them useful in the development of high-performance sensors that are sensitive to their chemical, mechanical, or physical environment. SWCNTs have also been shown to have excellent emission characteristics such as a low threshold field for emission and a high current density, because of their geometry, high aspect ratio, and small tip radius of curvature, as well as their high chemical and mechanical stability. These properties make them attractive as potential cold cathode emitters for field-emission displays (FEDs) [1–4]. Therefore, SWCNTs are promising candidates for use in field emitters and chemical sensors. SWCNTs also combine strength and flexibility, so they are excellent candidates for flexible electronic components. The very small lateral dimensions and superhigh Young's modulus enable SWCNTs to withstand very small bending radii and very high strains (e.g., elongation strains at the break point of about 30% and threshold strains for intratube electronic scattering of 5–10%) [5]. As a result, SWCNTs can be bent repeatedly to certain levels without changing their electrical properties.

This characteristic associated with SWCNTs is useful for their implementation in flexible electronic devices. Various methods have been reported for placing SWCNTs on flexible substrates, such as spraying (or casting) SWCNTs from aqueous solution, AC dielectrophoresis, and dry transfer printing [6]. However, these methods are not always the optimal ways, or even effective ways, of fabricating flexible devices. SWCNT films have been fabricated by spray coating the suspension onto plastic substrates of polyethylene naphthalate (PEN), polyethersulfone (PES), or polyarylate (PAR) using a conventional airbrush [7]. This method has certain disadvantages such as the use of organic solvents that are incompatible with the plastic substrates. For example, *N*,*N*-dimethylformamide (DMF) is known as the best solvent for making a stable suspension of SWCNT dispersion. However, DMF deforms the plastic substrate during spray coating. In addition, the technique requires chemical modification or thermal treatment at a high temperature after deposition of the SWNCT films on the plastic substrate, which may degrade the quality of the

substrate. Another problem is adhesion between the SWCNT film and the plastic substrate. Since the adhesion of SWCNTs to a plastic substrate is very poor, plastic substrates are coated with a polyimide (PI) or a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTS) prior to CNT deposition [7]. However, this procedure does not solve the adhesion problem completely.

In this study, we describe an extremely simple method for the fabrication of SWCNT-based flexible devices. In order to improve the adhesion of the SWCNT films, the transfer process is carried out using polydimethylsiloxane (PDMS) as the flexible substrate, instead of conventional plastic substrates such as PET or PES. We demonstrate the potential of SWNCT-based flexible gas sensors created using this method. In the same way, we attempt to develop a simple mass-fabrication method using the PDMS substrate without an organic binder, in order to achieve stable field emission.

**2 Experiment** Figure 1 illustrates the transfer method for the fabrication of flexible sensors and field emitters. First, a suspension of SWCNTs and an appropriate solvent was applied by spray coating onto a rigid substrate such as a Si wafer. SWCNT powder (purchased from Hanhwa Nanotech Co., Ltd.) with a diameter of 5–10 nm and an average length of 5–20 μm and ≈95% purity (prepared by CVD) was used. Prior to the SWCNT manipulation, the sample (1 mg) was dispersed ultrasonically (power of 200 W with a pulse cycle of 1 s ON and 1 s OFF for 1 h) in a DMF solution (100 mL) to form a suspension. The resulting solution was diluted to 0.01 mg/mL. The SWCNT solution was dispersed by spraying it onto the Si substrate on a hot plate with a temperature of ≈180 °C to remove the DMF solution (boiling point of DMF = 154 °C). The obtained films were then subjected to heat treatment at 350 °C for 1 h. The SWCNTs dispersed in DMF required this heat treatment to eliminate the DMF adsorbed on the surface of the SWCNTs. If the SWCNT films were deposited onto the surface of the plastic substrate directly by means of the spray-coating method, it would not be possible to carry out the heat treatment at such a temperature. The process used ensured good-quality SWCNT deposition on the substrate. The density of the SWCNTs across the films could be adjusted by varying the SWCNT concentration in the DMF solution. In the fabrication of flexible sensors, a pair of interdigitated Au electrodes was created using conventional photolithography methods with finger widths of 10 μm and gap sizes of 10 μm. A 10-μL volume of SWCNT solution was then deposited onto the Au interdigitated electrodes by spray coating to ensure good-quality deposition of the SWCNTs on the substrate.

Polydimethylsiloxane was used as the flexible substrate instead of a conventional flexible substrate such as PI or PES. PDMS is a Si-based organic polymer that has found wide applications in microelectromechanical system (MEMS) and microfluidic device fabrication, soft lithography, contact-lens manufacturing, and device encapsulation [8]. In its raw form, PDMS is a highly viscous flowing liquid, but is still optically transparent. Curing agents are added to this PDMS to give it structural rigidity. During the curing process, we found a form of PDMS with an adhesive property that occurred just before complete hardening; this form of PDMS looked like an adhesive tape. Therefore, the SWCNT films on Si substrates were transferred to the PDMS surface just before its complete hardening. In this state, the adhesive property of the PDMS caused the SWCNTs to adhere to it. Then, the PDMS with SWCNTs was hardened (cured) completely to ensure strong adhesion between the SWCNTs and the PDMS substrate.

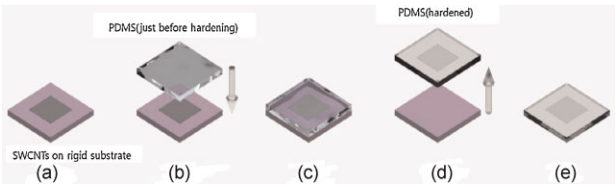


**Figure 1** (online color at: www.pss-a.com) Schematic of the process: (a) deposition of SWCNT films on rigid substrate using spray-coating method, (b) an adhesive property that occurred just before complete hardening; this form of PDMS looked like an adhesive tape, (c) curing process, (d) the adhesive property of the PDMS caused the SWCNTs to adhere to SWCNT films, (e) SWCNT films on flexible substrate.

**3 Results and discussions** The assembled devices from all four samples were exposed to 4-ppm $NO_2$. The initial resistance of the samples was a few hundred ohms after heat treatment. We carried out *in situ* measurement of the electrical resistance using the cycling chamber atmosphere from $NO_2$ to a vacuum at room temperature. The gas was introduced at a pressure of $5 \times 10^{-3}$ Torr in the vacuum system. The resistance of the suspended SWCNTs was measured using a Keithley 2400 series source meter, which recorded the electrical resistance as a function of the operating temperature.

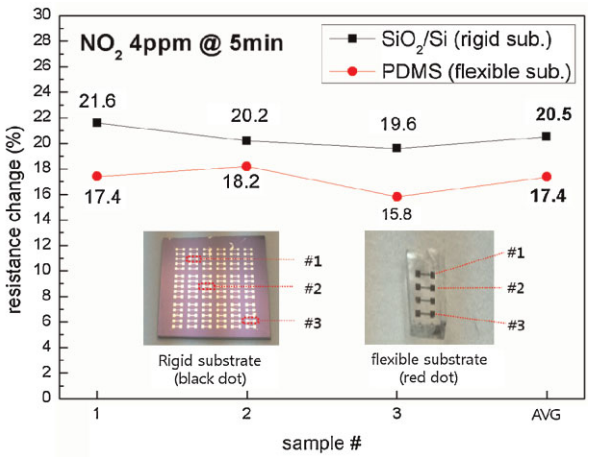


**Figure 2** (online color at: www.pss-a.com) Resistance response of the SWCNT films on $Si/SiO_2$ rigid substrate and PDMS flexible substrates to 4-ppm $NO_2$ at room temperature. Inner pictures show the samples of conventional rigid substrate based SWCNTs sensors and transferred SWCNTs sensors on the PDMS substrate.

Figure 2 shows the typical resistance response of the SWCNT films on flexible substrates to 4-ppm $NO_2$ at room temperature. During the test, a constant voltage (1 V) was applied between the electrodes. The response and recovery times were recorded during two short exposures to 4-ppm $NO_2$ gas in a vacuum at room temperature. Exposure to $NO_2$ rapidly decreased the resistance of the SWCNT network on the flexible substrate. The SWCNT films significantly affected the sensitivity and reversibility of the sensors towards $NO_2$.

Generally, exposure to $NO_2$ rapidly decreases the resistance of the SWCNTs. Similar behavior has been observed with individual SWCNT sensors. The response of the sensor is defined as $\Delta R/R_0 = (R–R_0)/R_0$, where $R_0$ is the resistance before exposure to $NO_2$ and $R$ is the maximum resistance during exposure. Theoretical and experimental studies have attributed this to charge transfer from the electron-accepting $NO_2$ molecule to the SWCNTs. Because the semiconducting SWCNTs are hole doped from environmental molecular oxygen, this charge transfer decreases the resistance of the SWCNT network by refilling the valence band of the semiconducting SWCNTs. The lower response of the SWCNTs compared to the previously reported results (~20%) can be explained by the different sensor configuration [9]. The measurements reported previously were conducted on selected semiconducting SWCNTs, whereas in the random network of nonfunctionalized SWCNTs in our sensor, both metallic and semiconducting nanotubes were present. The charge transfer from $NO_2$ to metallic nanotubes would not be expected to induce large changes in the sensor resistance. Gas-sensing characterizations of SWCNTs showing p-type semiconducting properties have been carried out [10].

The mechanical bendability of the as-fabricated sensors represents an important parameter for applications that are difficult or impossible to achieve with traditional sensors on rigid substrates [11]. Figure 3 compares the responses of a flexible sensor to 4-ppm $NO_2$ in vacuum when it was laminated on a flat surface (trace with squares) and when it was bent into a curved profile with a bending radius of 2 cm. In general, the sensing behaviors of the flexible sensor devices were quite reproducible. The average response during the first five minutes after exposure was 17.4% in the SWCNT films and 15.9% after sensor bending. The minor difference between the two characteristic traces indicates that bending of the sensor did not affect its sensing performance significantly, i.e., after bending, there was no change in response time and only a slight decrease in sensitivity.

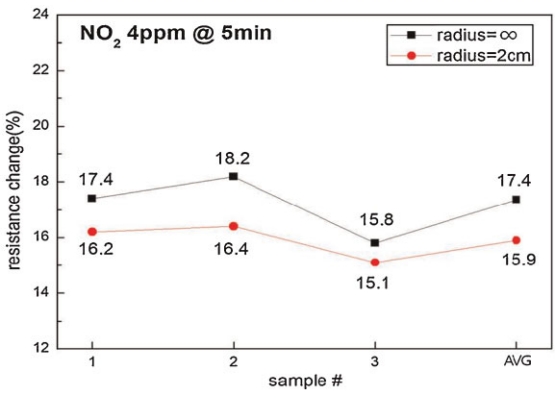


**Figure 3** (online color at: www.pss-a.com) Comparison of the responses of a flexible sensor to 4-ppm $NO_2$ in vacuum when it was laminated on a flat surface (trace with squares) and when it was bent into a curved profile with a bending radius of 2 cm.

However, the sensitivity was lower than that of a conventional SWCNT-film-based sensor on a rigid substrate. The unsorted SWCNT-film-based sensor on a rigid substrate was reported to have a sensitivity of 25% in our previous work. The significantly lower response of the SWCNTs here compared to the previously reported results can again be explained by the different sensor configuration. In this transfer method, the viscosity of PDMS meant that the SWCNTs were stuck mechanically before hardening. Therefore, many carbon nanotubes were stuck to the PDMS substrate, so the sensing area was reduced. Another obstacle was that only a few layers of SWCNTs were transferred onto the substrate. Therefore, the resistance of the base line was larger than that of the SWCNT film on a rigid substrate. This also caused a lower sensitivity than that of the rigid substrate. However, in our work, we attempted to develop a simple mass-fabrication method using a flexible substrate such as PDMS.

Single-walled carbon nanotube films were first deposited on rigid substrates such as a Si wafer or glass using the spray method. In this case, the electrical properties of the SWCNTs can be enhanced by acidic and thermal treatments. In the same way as described above, the SWCNT film on a rigid substrate was also transferred to a PDMS substrate. Then, as the surface treatment, the processes of rubbing and peel-off with adhesive tape were carried out after complete transfer, to cause the SWCNT emitters to protrude from the PDMS surface for efficient electron emission [12]. The SEM images in Fig. 4 show the surface morphology of the SWCNT emitters after transfer to the PDMS substrate. The adhesive tape was applied to the surface of the transferred SWCNTs on the PDMS substrate. During removal of the tape, tensile forces perpendicular to the surface were applied to the

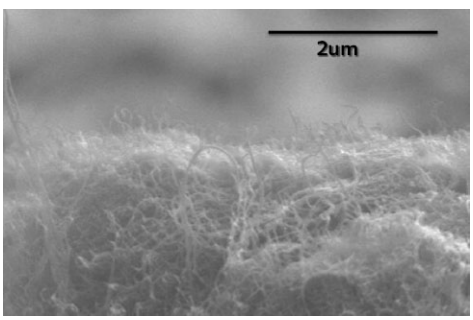


**Figure 4** Cross-sectional FE-SEM image of the transferred SWCNTs on the PDMS substrate.

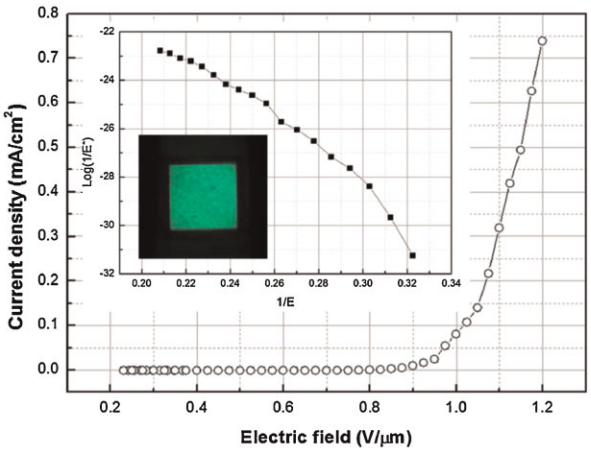


**Figure 5** (online color at: www.pss-a.com) *I–V* curve and F–N plots (inner) of the SWCNT emitters on PDMS substrate.

SWCNTs, thereby inducing the observed SWCNT orientation [13]. The field-emission properties of the dispersed SWCNT emitters were tested in a diode configuration under a vacuum of $5 \times 10^{-5}$ Torr. The anode and cathode were separated by 270 μm. In order to image the electron emission site, we placed a phosphor/ITO/glass assembly at the anode side.

Figure 5 shows the *I–V* characteristics of the electron emissions from the diode-type SWCNT emitters on the PDMS substrate. In the case of SWCNT emitters on the PDMS substrate, the turn-on field was shown to be as low as about 0.9 V/μm, and the emission current density was about 0.75 mA/cm$^2$ at a field of 1.2 V/μm. The inset shows the field-emission-site density image and Fowler–Nordheim (F–N) plot of the SWCNTs on the PDMS. As expected, the part with the well-aligned SWCNTs had an excellent emission pattern, showing homogeneous emission over the whole area.

Although it is a very crude approximation, the F–N formula is still frequently used as a mathematical interpretation of field emission:

$$J = \frac{1.56 \times 10^{-6} E^2}{\phi} \exp\left(-\frac{6.38 \times 10^{7} \phi^{3/2}}{E}\right),$$

where $J$ is the field-emission current density (in A/cm$^2$), $\phi$ is the work function (in eV), and $E$ is the local electric field at the emission sites (in V/cm). The actual value of $E$ could not be measured directly. It is related to the applied voltage, $V$, by setting, where $d$ is the anode–cathode separation and $\beta$ is the so-called enhancement factor of the field. $\beta$ depends on the emitter geometry for tip-like structures, and can be determined from the aspect ratio of the emitter. The electric field, directly calculated by $V/d$, is termed the "apparent electric field" to distinguish it from the actual local field, at the emission sites [14, 15]. Figure 5 (inner) shows the F–N plots, the linearity of which indicates that the *I–V* characteristics are governed by a conventional field-emission mechanism. This linearity is explained by the increase in perpendicularly well-protruded SWCNTs without organic materials in the paste.

**4 Conclusion** In conclusion, the deposition of SWCNTs on flexible substrates through a simple transfer process has been demonstrated, and has been used to fabricate high-performance $NO_2$ sensors with excellent mechanical flexibility. Typical flexible sensors exhibited a sensitivity of ~17% for 4-ppm $NO_2$ in a vacuum at room temperature. The performance of the devices was reduced slightly to ~16% when they were bent to a curved profile with a bending radius of 2 cm. The characteristics of the flexible gas sensors suggest that they are promising candidates for applications that demand fast and sensitive detection under conditions where conformal wrapping over curvilinear surfaces, high tolerance toward repeated bending, and mechanical shock resistance, for example, are required. The field emitter fabricated using the above transfer method had excellent electron-emission properties. The turn-on field was less than 0.9 V/μm, and the emission current density approached 0.75 mA/cm$^2$ at 1.2 V/μm. Consequently, a drastic increase in the field-emission current, excellent uniformity of the emission site, and a decrease in the turn-on voltage were achieved. These results may enable us to produce a carbon-nanotube-based field-emission device in the future. In our work, we attempted to develop a simple mass-fabrication method without an organic binder for a stable field-emission device on a flexible substrate. There are many advantages of the flexible substrate, including the lower cost of production of the emitter and the possibility of making emitters of any geometry or shape for use in any electrical application.

**Acknowledgements** This work was supported by World Class University (WCU, R32-2008-000-10082-0) Project of the Ministry of Education, Science, and Technology (Korea Science and Engineering Foundation) and the Industrial Core Technology Development program funded by the Ministry of Knowledge Economy (no. 10037394). Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (CAFDC-20120000816).

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