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Modulation-Doped Multiple Quantum Wells of Aligned Single-Wall Carbon Nanotubes

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Heterojunctions, quantum wells, and superlattices with precise doping profiles are behind today's electronic and photonic devices based on III–V compound semiconductors such as GaAs. Currently, there is considerable interest in constructing similar artificial 3D architectures with tailored electrical and optical properties by using van der Waals junctions of low-dimensional materials. In this study, the authors have fabricated a novel structure consisting of multiple thin (≈20 nm) layers of aligned single-wall carbon nanotubes with dopants inserted between the layers. This "modulation-doped" multiple-quantum-well structure acts as a terahertz polarizer with an ultra-broadband working frequency range (from ≈0.2 to ≈200 THz), a high extinction ratio (20 dB from ≈0.2 to 1 THz), and a low insertion loss (<2.5 dB from ≈0.2 to 200 THz). The individual carbon nanotube films—highly aligned, densely packed, and large (2 in. in diameter)—were produced using vacuum filtration and then stacked together in the presence of dopants. This simple, robust, and cost-effective method is applicable to the fabrication of a variety of devices relying on macroscopically 1D properties of aligned carbon nanotube assemblies.

1. Introduction

Doping, alloying, and combining traditional semiconductors are at the core of today's technologies, including computers, laser diodes, and smart phones.[1–3] Over the last few decades, considerable progress has been made in the growth and basic studies of individual nano-objects such as quantum dots,[4] carbon nanotubes,[5,6] graphene,[7,8] and transition metal dichalcogenides.[9,10] Combining and hybridizing these low-dimensional building blocks can lead to an unprecedented degree of controllability in materials properties, in a manner similar to what has traditionally been realized in the band gap engineering of III–V compound semiconductor heterostructures.[11–13] By controlling alloy compositions and layer thicknesses, one can quantum engineer wave functions, energy levels, and optical transition strengths for specific applications. In addition, precise control of the levels and locations of dopants is crucial for realizing the desired carrier densities and distributions within such devices.

Here, we have assembled individual single-wall carbon nanotubes (SWCNTs) into a macroscopically organized structure comprised of stacked conducting layers of highly aligned and densely packed SWCNTs. The individual layers were ≈20 nm in thickness and 2 in. in diameter, containing SWCNTs that spontaneously aligned during vacuum filtration.[14] Dopants were incorporated into the structure in such a way that they reside between the conducting layers, effectively increasing the conductivity of the layers, à la modulation doping[15] (also known as remote doping) which is used, e.g., in high-mobility field-effect transistors.[16] This unique 3D architecture of doped SWCNTs exhibited excellent performance as a terahertz (THz) polarizer with an ultra-broadband working frequency range (from ≈0.2 to ≈200 THz), a high extinction ratio (ER) (20 dB from ≈0.2 to 1 THz), and a low insertion loss (IL) (<2.5 dB from ≈0.2 to 200 THz), exceeding the performance of previously reported THz polarizers using SWCNTs.[17–19] Our basic fabrication procedure is general and can in principle be extended with no limitations in size and complexity to achieve more complicated and larger structures containing aligned SWCNTs.

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2. Results and Discussion

We used a 2 in. vacuum-filtration system (**Figure 1**a) with a 200 nm pore-size filter membrane to filter a prepared SWCNT suspension under a well-controlled manner (see the Experimental Section), which left SWCNTs uniformly on the filter membrane (Figure 1b). Figure 1c shows a scanning electron

microscopy image of a produced film transferred onto a SiO$_2$/Si substrate, exhibiting densely packed, aligned SWCNTs, similar to the films reported earlier using a 1 in. filtration system.[14] The film absorbance at a wavelength of 660 nm is strongly polarization dependent, as shown in Figure 1d (a 1 in. film) and Figure 1e (a 2 in. film); here, the absorbance values are normalized to the value for the parallel polarization. Figure 1f presents
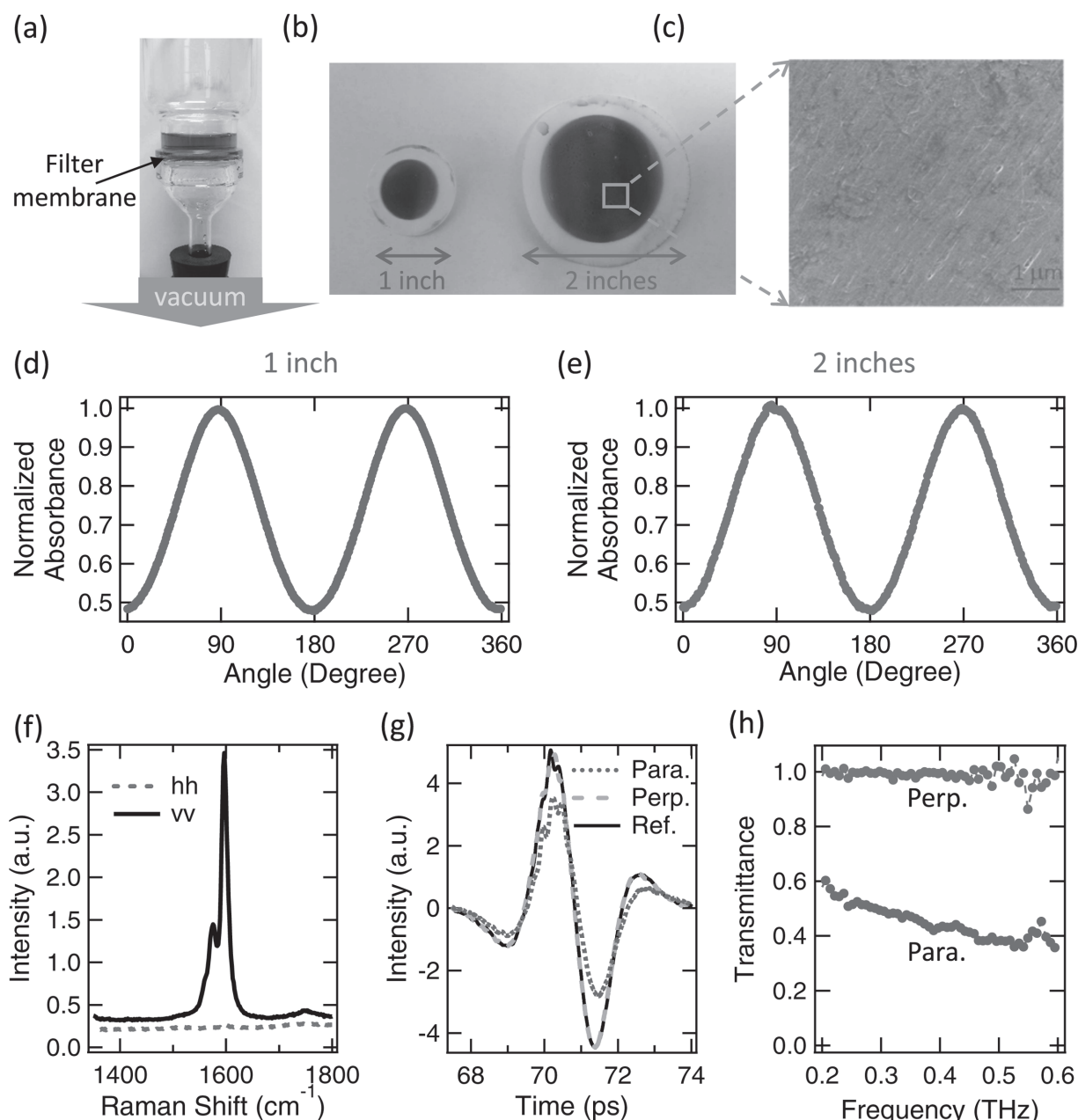

Figure 1. Fabrication and characterization of aligned SWCNT films. a) Vacuum filtration system connected with a vacuum pump. The filtration speed has to be slow and well-controlled to achieve spontaneous alignment.[14] b) Wafer-scale SWCNT films produced on filter membrane. c) A scanning electron microscopy image of an aligned and highly packed SWCNT film. Angular dependence of transmittance at a wavelength of 660 nm for d) a 1 in. film and e) a 2 in. film; the absorbance values are normalized to the value for the parallel polarization. f) Polarized Raman spectra for a 23 nm thick aligned SWCNT film in two polarization configurations. g) Time-domain waveforms of THz radiation transmitted through the reference intrinsic Si substrate and the aligned SWCNT film for parallel and perpendicular polarizations. h) Transmittance spectra for parallel and perpendicular polarizations.

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polarized Raman spectra for a 23 nm thick aligned film (Figure S1, Supporting Information) of arc-discharge SWCNTs with an average tube diameter of 1.4 nm, taken with an excitation laser wavelength of 532 nm in two polarization configurations (I_{VV} and I_{HH}).[20] From these polarized Raman spectra, we calculated the nematic order parameter, S, of this film to be ≈1, i.e., near-perfect alignment (see the Supporting Information).[20]

Figure 1g shows THz time-domain waveforms transmitted through a reference intrinsic Si substrate and the SWCNT film transferred onto an intrinsic Si substrate, for THz polarization parallel and perpendicular to the SWCNT alignment direction. The transmittance for the perpendicular case essentially overlaps that for the reference, indicating thethat re is no attenuation by the SWCNT film. On the other hand, the signal drops dramatically in the parallel case, suggesting that there is a strong attenuation. Figure 1h displays the transmittance spectra calculated from Fourier transformation of the time-domain

data in Figure 1g, exhibiting significant optical anisotropy. The transmittance is almost 1 in the perpendicular configuration and quite small (0.4–0.6) in the parallel configuration due to the interplay between Drude absorption and plasmon absorption,[21] showing strong polarization dependence. Also, the value of S calculated from this data[17] is ≈1, in agreement with the Raman data (see the Supporting Information). Note that the THz beam size is ≈mm^2, thus probing a macroscopic area. The unity nematic order parameter calculated from the THz transmittance data reflects the global alignment structure in our produced film, which was confirmed through scanning electron microscopy images as well (Figure S2, Supporting Information).

To further increase the value of ER, we combine multiple films vertically by stacking, while inserting dopants between layers at the same time (**Figure 2**). First, a 2 in. sized aligned SWCNT film was cut into four square-shaped pieces using a pair of scissors (Figure 2a). Each piece was ≈8 mm^2, still larger
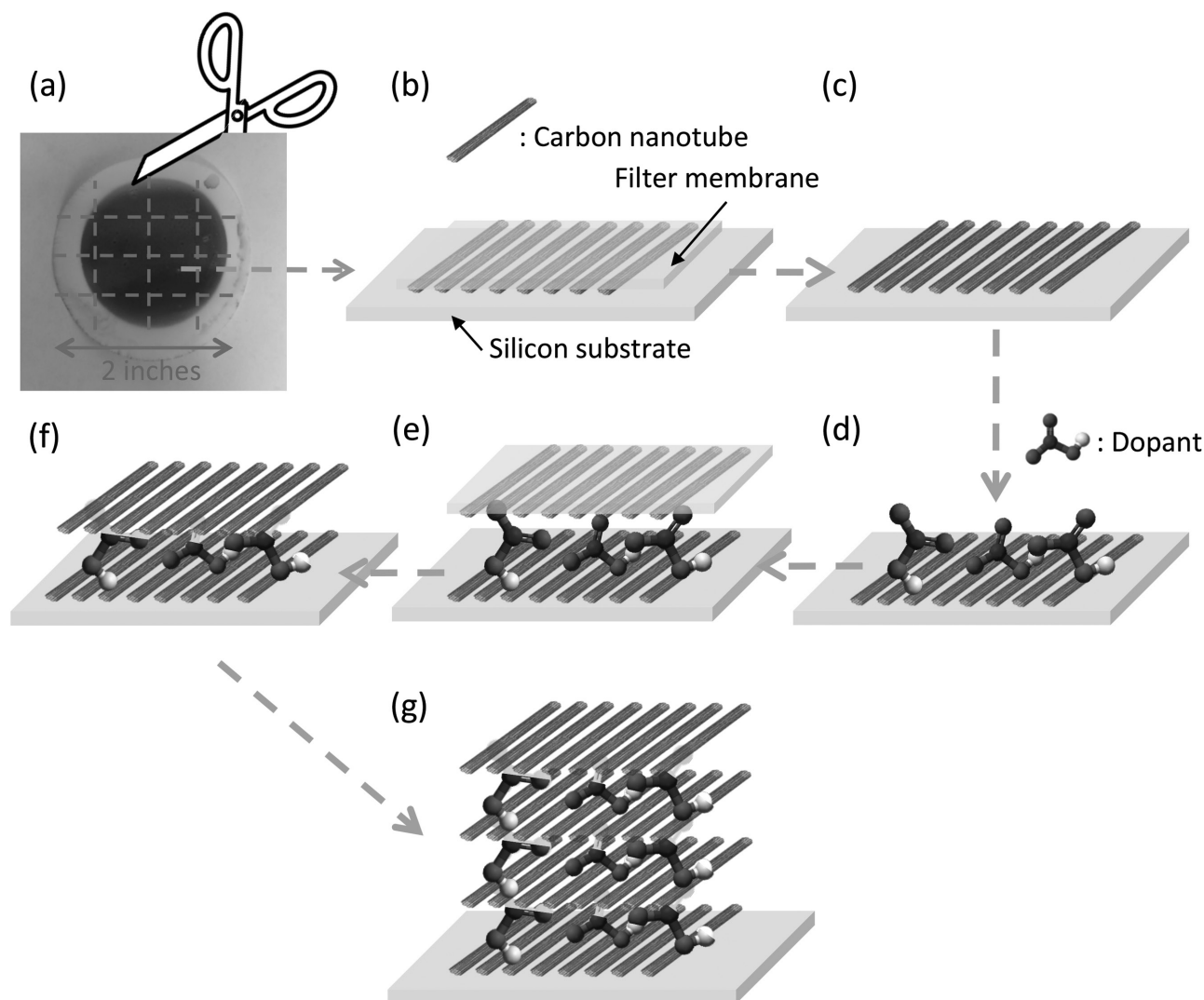

Figure 2. Schematic diagram of the SWCNT film stacking-doping procedure. a) A 2 in. sized aligned SWCNT film was cut into four square-shaped pieces using a pair of scissors. b,c) The first piece was transferred onto an intrinsic Si wafer. d) The transferred film was chemically doped by nitric acid. e,f) The second piece was manually stacked and transferred on top of the first doped piece. g) The processes (a–f) were repeated four times to make a modulation-doped multiple-quantum-well structure.

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than the THz beam size. We then placed one piece on an intrinsic Si wafer (Figure 2b) and dissolved the filter membrane using an organic solvent (N-methyl-2-pyrrolidone or chloroform) to transfer the first layer onto the substrate (Figure 2c). The film was thoroughly washed by acetone and gently air-dried. The transferred film was then immersed into 68% concentrated nitric acid bath for 2 h to be made strongly p-doped (Figure 2d). Since CNTs in our film are globally aligned along the same direction, the adjacent piece to the first doped piece was chosen and stacked manually on top of the first one, with careful control to make the common edge between the two pieces as parallel as possible (Figure 2e). The filter membrane was then dissolved using the same organic solvent (Figure 2f). This stacking-doping process was repeated for up to four layers (Figure 2g). The chemical doping process can be done with other acids as well: H_2SO_4,[22,23] $NH_4S_2O_8$,[23] HCl,[22] H_2SO_3,[24] iodine solution,[24] and benzyl vilogen.[25]

The ER value is defined as $-\log (T_{\parallel}/T_{\perp})$, where $T_{\parallel}$ ($T_{\perp}$) is the transmittance for the parallel (perpendicular) polarization and

was calculated after each stacking step, as shown in **Figure 3**a. The ER value increases dramatically and linearly with increasing number of stacking layers, which is equivalent to the total thickness of the structure (Figure S1, Supporting Information). The linearly increasing ER, shown in Figure 3b, suggests that perfect alignment and dense packing are well preserved during the stacking and wet transfer process (Figures S1 and S3, Supporting Information). In principle, the stacking process can be repeated indefinitely, only limited by the lateral size of the film, which can be increased by increasing the size of the filtration system. Nitric acid doping typically introduces a large density of holes, shifting the Fermi energy downward into the valence band, which dramatically increases the parallel conductivity through free-carrier absorption (and thus the ER) in the THz range, as shown in Figure 3c. Furthermore, Figure 3d shows that the ER peak before doping at ≈170 THz, corresponding to the E_{11} exciton absorption in semiconducting SWCNTs, is not observable after doping due to Pauli blocking;[22,26] overall, doping has extended the working frequency range of our
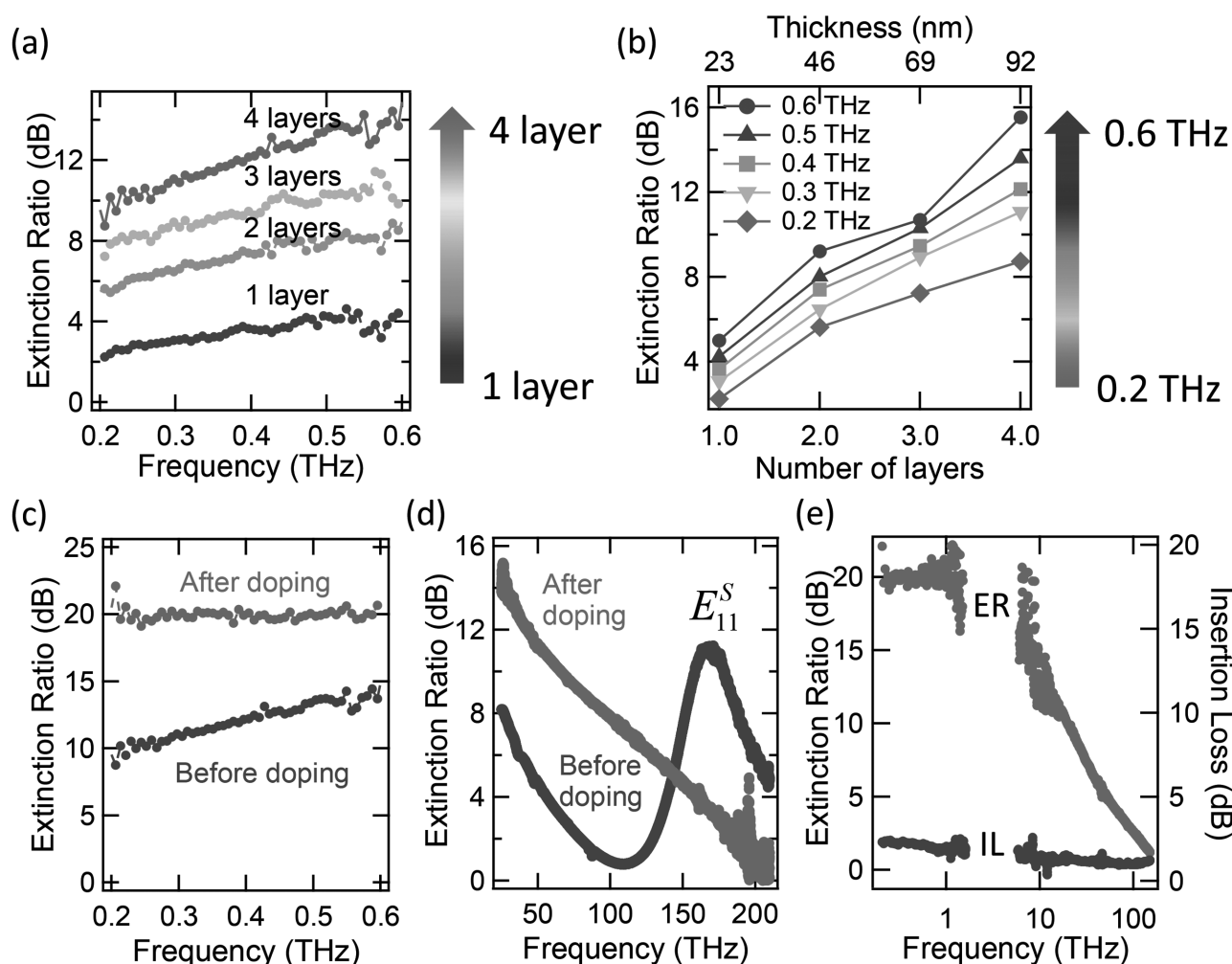
Figure 3. Effects of stacking and doping on the THz and mid-infrared response of aligned SWCNT films. a) ER versus frequency in the THz range for 1–4 layers. b) ER versus the number of layers at different frequencies in the THz range. The corresponding rate of increase in ER with thickness (see the top axis) is ≈120 dB μm^{-1}. c) ER spectra in the THz region after doping and before doping. d) ER spectra in the mid-infrared region after doping and before doping. The E_{11} exciton peak in semiconducting SWCNTs vanishes due to doping (Pauli blocking). e) ER and IL of stacked, modulation-doped aligned SWCNT films in the range of 0.2–200 THz. The frequency axis is on a logarithmic scale.

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polarizer significantly up to ≈200 THz. Finally, Figure 3e shows both ER and IL (–log (T⊥)) of stacked and modulation-doped aligned SWCNT films in an ultra-broad spectral range—from ≈0.2 to 200 THz. The ER value is consistently high (20 dB from ≈0.2 to 1 THz), while the IL value is extremely low (less than 2.5 dB from ≈0.2 to 200 THz) in the whole spectral range.

3. Conclusion

In conclusion, we developed a simple, robust, and cost-effective method for fabricating 3D architectures of aligned and modulation-doped single-wall carbon nanotubes. Specifically, by stacking and chemically doping highly aligned, densely packed single-wall carbon nanotube films produced by a vacuum filtration method using a 2 in. filtration system, we made an organized macroscopic object that is anisotropically conducting. We demonstrated the utility of the fabricated structure by terahertz and mid-infrared spectroscopy, showing ultra-broadband polarizer performance from ≈0.2 to 200 THz with an extinction ratio value of up to 20 dB in the THz range and an insertion loss value of less than 2.5 dB in the entire spectral range. This stacking and doping process can be applied with no limitations in size and thickness in principle and can be easily tailored for different application scenarios.

4. Experimental Section

Sample Preparation: A macroscopically aligned SWCNT film was prepared, first by pouring a solution of well-dispersed arc-discharge P2-SWCNTs (Carbon Solutions, Inc. USA) with dilute SWCNTs and sodium deoxycholate surfactant (below critical micelle concentration) through a 2 in. diameter vacuum filtration system. A polycarbonate filter membrane (Nuclepore track-etched polycarbonate hydrophilic membranes) with a pore size of 200 nm and a 2 in. diameter was used. The filtration speed was kept low but was accelerated at the end of the filtration process to quickly dry the film. Then, the system was pumped for an additional 15–30 min to completely dry the film. The detailed procedures can be found in ref. [14].

Microscopy and Spectroscopy Characterization: Microscopic alignment structures of the aligned films were examined by a scanning electron microscope (JEOL 6500F scanning electron microscope), and the film thicknesses were measured by an atomic force microscope (Bruker Multimode 8). The polarized Raman spectra were taken by using a commercial Renishaw inVia Raman microscope. The stacked CNT polarizer performance was characterized by using a commercial terahertz time-domain transmission spectroscopy system (Advantest TAS7500TS) and a Fourier transform infrared spectroscopy setup (JASCO FT/IR-660).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

[1] Z. I. Alferov, *Semiconductors* **1998**, *32*, 1.
[2] S. L. Chuang, *Physics of Photonic Devices*, John Wiley & Sons Inc., Hoboken, New York **2009**.
[3] S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, John Wiley & Sons Inc., Hoboken, New York **2006**.
[4] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[5] S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603.
[6] P. J. F. Harris, *Carbon Nanotube Science: Synthesis, Properties and Applications*, Cambridge University Press, Cambridge **2011**.
[7] K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, A. Firsov, *Science* **2004**, *306*, 666.
[8] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
[9] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, *7*, 699.
[10] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, *6*, 147.
[11] A. K. Geim, I. V. Grigorieva, *Nature* **2013**, *499*, 419.
[12] X. Wang, F. Xia, *Nat. Mater.* **2015**, *14*, 264.
[13] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. C. Neto, *Science* **2016**, *353*, aac9439.
[14] X. He, W. Gao, L. Xie, B. Li, Q. Zhang, S. Lei, J. M. Robinson, E. H. Hároz, S. K. Doorn, W. Wang, R. Vajtai, P. M. Ajayan, W. W. Adams, R. H. Hauge, J. Kono, *Nat. Nanotechnol.* **2016**, *11*, 633.
[15] R. Dingle, H. L. Störmer, A. C. Gossard, W. Wiegmann, *Appl. Phys. Lett.* **1978**, *33*, 665.
[16] T. Mimura, *IEEE Trans. Microwave Theory Tech.* **2002**, *50*, 780.
[17] L. Ren, C. L. Pint, L. G. Booshehri, W. D. Rice, X. Wang, D. J. Hilton, K. Takeya, I. Kawayama, M. Tonouchi, R. H. Hauge, J. Kono, *Nano Lett.* **2009**, *9*, 2610.
[18] L. Ren, C. L. Pint, T. Arikawa, K. Takeya, I. Kawayama, M. Tonouchi, R. H. Hauge, J. Kono, *Nano Lett.* **2012**, *12*, 787.
[19] A. Zubair, D. E. Tsentalovich, C. C. Young, M. S. Heimbeck, H. O. Everitt, M. Pasquali, J. Kono, *Appl. Phys. Lett.* **2016**, *108*, 141107.
[20] C. Zamora-Ledezma, C. Blanc, M. Maugey, C. Zakri, P. Poulin, E. Anglaret, *Nano Lett.* **2008**, *8*, 4103.
[21] Q. Zhang, E. H. Hároz, Z. Jin, L. Ren, X. Wang, R. S. Arvidson, A. Lüttge, J. Kono, *Nano Lett.* **2013**, *13*, 5991.
[22] R. Graupner, J. Abraham, A. Vencelova, T. Seyller, F. Hennrich, M. M. Kappes, A. Hirsch, L. Ley, *Phys. Chem. Chem. Phys.* **2003**, *5*, 5472.
[23] H. Tantang, J. Y. Ong, C. L. Loh, X. C. Dong, P. Chen, Y. Chen, X. Hu, L. P. Tan, L. J. Li, *Carbon* **2009**, *47*, 1867.
[24] V. Skakalova, A. B. Kaiser, U. Dettlaff-Weglikowska, K. Hrncarikova, S. Roth, *J. Phys. Chem. B* **2005**, *109*, 7174.
[25] X. He, N. Fujimura, J. M. Lloyd, K. J. Erickson, A. A. Talin, Q. Zhang, W. Gao, Q. Jiang, Y. Kawano, R. H. Hauge, F. Léonard, J. Kono, *Nano Lett.* **2014**, *14*, 3953.
[26] F. Hennrich, R. Wellmann, S. Malik, S. Lebedkin, M. M. Kappes, *Phys. Chem. Chem. Phys.* **2002**, *5*, 178.