Nanotechnology

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Nanotechnology **20** (2009) 335705 (7pp) doi:10.1088/0957-4484/20/33/335705

Periodically striped films produced from super-aligned carbon nanotube arrays

Kai Liu[1,2], Yinghui Sun[1], Peng Liu[1], Jiaping Wang[1], Qunqing Li[1], Shoushan Fan[1] and Kaili Jiang[1]

[1] Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, People's Republic of China
[2] Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: jpwang@tsinghua.edu.cn

Received 13 May 2009, in final form 2 July 2009
Published 28 July 2009
Online at stacks.iop.org/Nano/20/335705

Abstract

We report a novel way to draw films from super-aligned carbon nanotube arrays at large drawing angles. The obtained super-aligned carbon nanotube films have a periodically striped configuration with alternating thinner and thicker film sections, and the width of the stripes is equal to the height of the original arrays. Compared with ordinary uniform films, the striped films provide a better platform for understanding the mechanism of spinning films from arrays because carbon nanotube junctions are easily observed and identified at the boundary of the stripes. Further studies show that the carbon nanotube junctions are bottleneck positions for thermal conduction and mechanical strength of the film, but do not limit its electrical conduction. These films can be utilized as striped and high-degree polarized light emission sources. Our results will be valuable for new applications and future large-scale production of tunable super-aligned carbon nanotube films.

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1. Introduction

Carbon nanotube (CNT) films have attracted much attention due to their excellent performance in flexibility, transparency and conductivity [1]. Compared with solution-based methods for fabricating CNT films, e.g. filtration, dip coating and spray coating [1–6], drawing films directly from super-aligned CNT (SACNT) arrays in a dry state provides a convenient way to prepare large-scale CNT films [7–9]. The as-produced SACNT films are evidently distinguished from random CNT films [1–6] made from solution-based methods by their 'unidirectional' nature, i.e. CNTs in SACNT films are aligned parallel to the drawing direction, which have some unique applications such as polarizers and polarized light sources [7, 10, 11]. Crossed SACNT films are robust with abundant nanosized holes, which are good candidates for supporting films of micro-grids for transmission electron microscopy (TEM) [12]. Recently, SACNT films were used as flexible and stretchable thermo-acoustic loudspeakers due to their ultrasmall heat capacity per unit area [13]. The fast high temperature response of SACNT films induced their application in incandescence displays [14]. There is no doubt that more and more applications of SACNT films will be demonstrated in the future.

In order to further develop applications, better performance of SACNT films is required, and thus it is essential to clarify basic issues of SACNT films, among which the film formation mechanism and its effects on the film properties are two key issues. During the drawing process, intermittent bundling within the SACNT array is indispensable [10, 11] and CNTs are joined end-to-end forming CNT junctions in the SACNT film [15]. These CNT junctions evidently play an important role in understanding the film formation mechanism, and have non-negligible effects on the film properties. However, it is very hard to directly observe and identify these CNT junctions because they distribute randomly and immerse deeply in ordinary uniform SACNT films, which is also an obstacle to further studies of their effects on the film properties. Here, to overcome this deficiency, we report a novel way to draw SACNT films from SACNT arrays at large drawing angles (figure 1(a)). The SACNT films are composed of periodic stripes with

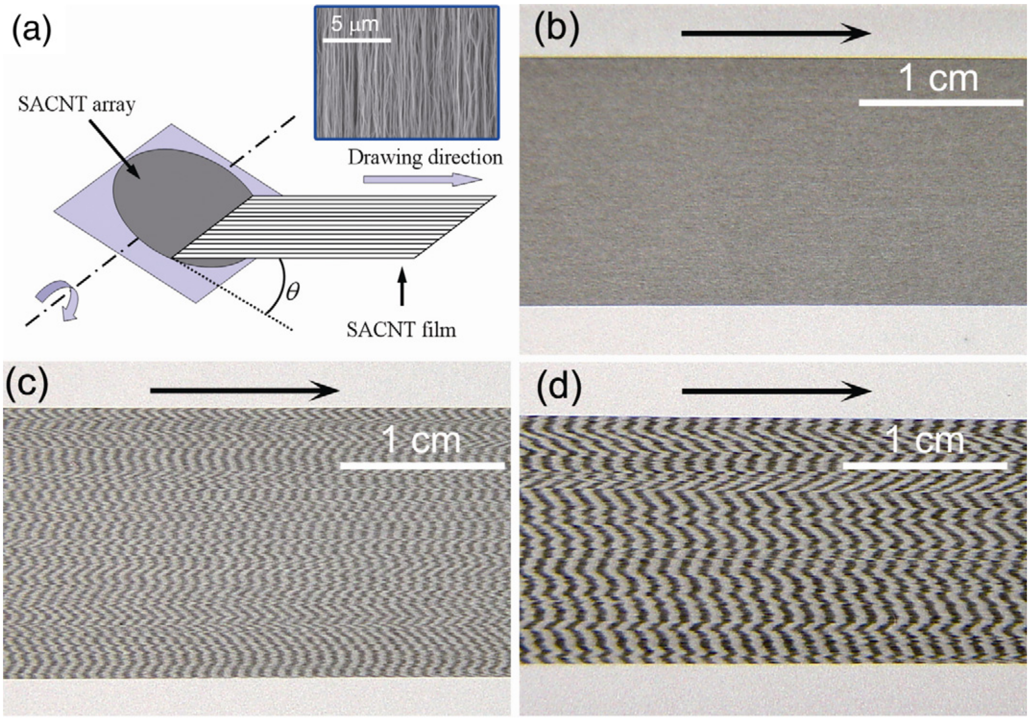

Figure 1. SACNT films produced at various drawing angles. (a) Illustration of producing films at a drawing angle of θ. The inset shows an SEM image of aligned CNTs in an SACNT array. (b)–(d) Photographs of three types of SACNT films on the same white pad taken by a digital camera. The black arrows indicate the drawing direction. The films were drawn from: (b) a 410 μm high SACNT array at a drawing angle of 5°; (c) a 410 μm high SACNT array at a drawing angle of 35°; (d) a 608 μm high SACNT array at a drawing angle of 35°.

alternating alignments of thick and thin film sections, and the width of the stripes is equal to the height of the SACNT array. Compared with ordinary uniform SACNT films, the striped SACNT films provide a better platform for understanding the mechanism of spinning SACNT films because CNT junctions are easily observed and identified at the boundary of the stripes. The formation mechanism of the stripes is clarified by *in situ* recording the drawing process. Further studies show that the CNT junctions are bottleneck positions for thermal conduction and mechanical strength of the SACNT film, but do not limit its electrical conduction. These films can be utilized as striped and high-degree polarized light emission sources.

2. Experimental investigation

2.1. Drawing films from SACNT arrays at various drawing angles

SACNT arrays were synthesized in batches by pyrolysis of acetylene on 4-inch silicon wafers with iron as catalyst [15]. By varying the growth time, SACNT arrays with different heights were obtained [11]. In this paper, the height of SACNT arrays is in the range of 230–610 μm. The film drawing apparatus includes a tunable tilted platform and a movable manipulator controlled by a computer. To draw an SACNT film, we first fixed a wafer with an SACNT array on the tilted platform, and preset this tilted platform so that the wafer plane and the horizontal plane formed an angle, θ. Then we used a glass plate covered with double-sided tape to stick to the SACNT array, fixed the glass plate on the manipulator, and controlled the manipulator to draw CNTs out from the wafer horizontally forming an SACNT film (figure 1(a)). The drawing speed is set at 5 mm s^{-1}. Therefore the SACNT film plane and the wafer plane also formed an angle of θ which was defined as the 'drawing angle' in the text. By varying the drawing angle θ in the range of 0°–35°, we obtained various types of SACNT films. At a very large drawing angle beyond 35°, the film usually cannot be continuously drawn out.

2.2. Measuring transmittances of dark and bright stripes

To measure the transmittances of dark and bright stripes, it is necessary to use a detector with a monitoring point whose diameter is smaller than the width of the dark or bright stripes. Here we used a tungsten lamp as the light source and an optical spectroradiometer (Konika Minolta CS-1000) as the detector to measure the spectra in the wavelength range from 380 to 780 nm. The size of the available and minimum monitoring point of the detector is about 500 μm in diameter. We measured the transmittances of the films drawn from a 608 μm high SACNT array at various drawing angles. In these films, the widths of dark and bright stripes are both equal to 608 μm, which are larger than the diameter of the monitoring point.

To carry out a measurement, we fixed and aligned the tungsten lamp and the optical spectroradiometer face to face, and recorded a spectrum as the source spectrum. After that we fixed a striped SACNT film on an adjustable translation platform and inserted them between the lamp and the spectroradiometer. At first we aligned the middle position of one bright stripe to the monitoring point of the

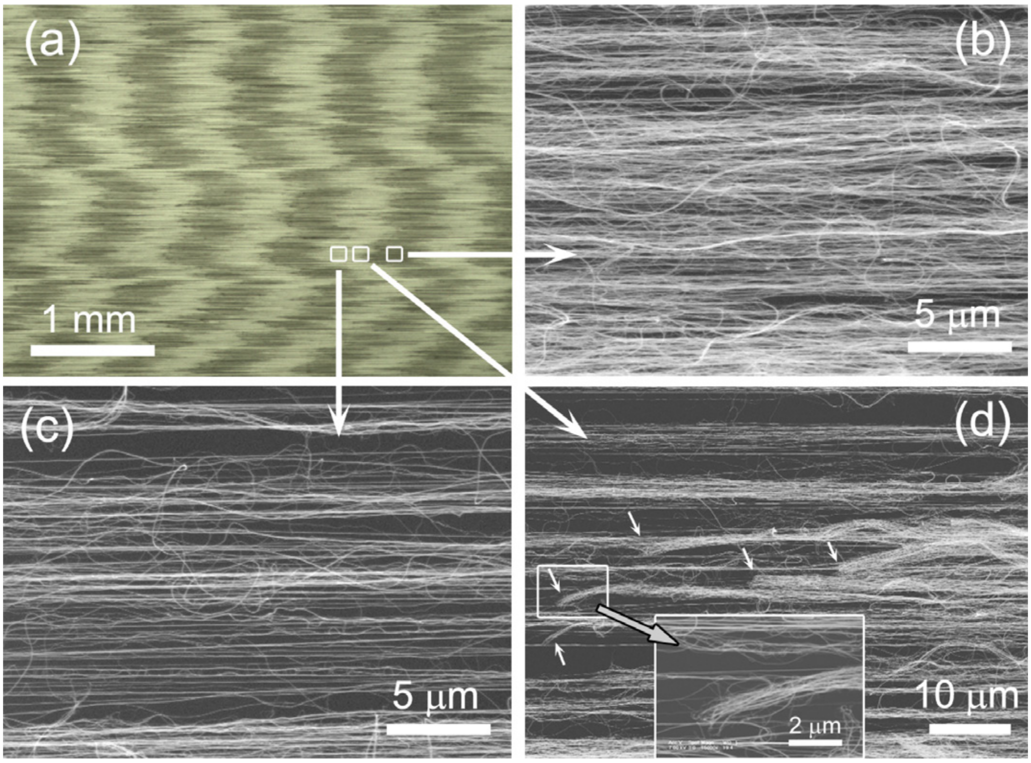

Figure 2. Optical and SEM images of a striped film drawn from a 410 μm high SACNT array at a drawing angle of 35°. (a) Optical image. (b) SEM image of a dark stripe. (c) SEM image of a bright stripe. (d) SEM image of the boundary between a dark stripe and a bright stripe. The small white arrows indicate some CNT junctions. The inset shows an enlarged image of a CNT junction.

spectroradiometer by the translation platform and recorded a spectrum. Then we moved the translation platform step by step with a step displacement of 608 μm, so that we aligned the middle positions of adjacent dark stripes and bright stripes alternately to the monitoring point and recorded the corresponding spectra. By comparing the source spectrum with the spectra after the lamp light transmitted the dark and bright stripes, we calculated the transmittances of the dark and bright stripes.

2.3. Measuring the mean transmittance of SACNT films

We measured the mean transmittance of SACNT films using a Perkin-Elmer Lambda 950 UV/vis spectrometer which provided a relatively large-size light source and monitoring point. The light source emitted a rectangular-shaped natural light with a size of about 10 mm (L) × 2 mm (W) at the center of the sample platform. We placed an SACNT film at the center of the platform with the drawing direction parallel to the long side of the light, so that the light area covered more than 15 stripes and thus the measuring results represented the mean transmittance of the film.

3. Results and discussions

The as-produced film is uniform in transparency when the drawing angle is small (figure 1(b)). Nevertheless, when the drawing angle is typically larger than 20°, the film becomes striped obviously, with alternating alignments of dark and bright stripes along the drawing direction (figures 1(c) and (d)). Films produced from higher SACNT arrays contain stripes with larger widths (figure 1(c) versus 1(d)). The dark and bright stripes can also be distinguished using a scanning electron microscope (SEM) or even an optical microscope (figure 2(a)). SEM images show that dark stripes consist of more CNT bundles compared to bright ones (figure 2(b) versus 2(c)), indicating that dark stripes of the film are thicker and more opaque. Interestingly, many CNT junctions are observed at the boundary between dark and bright stripes (figure 2(d)). These phenomena suggest that the drawing process at a large drawing angle should be distinguished from that at a small one.

To clarify the formation mechanism of the periodically striped films, we *in situ* recorded the drawing process at a large drawing angle using an optical microscope. As shown in movie S1 in the multimedia file (available at stacks.iop.org/Nano/20/335705), an obvious feature of the drawing process at a large drawing angle is that most of the CNT bundles in a local position have consistent behavior, i.e. moving together from the top to the bottom of the SACNT array, and then from the bottom back to the top, repeatedly. This drawing process evidently further supports the drawing model of end-to-end joining of CNTs [15].

As shown in figure 3, this cyclic process at a drawing angle θ can be simply divided into five steps: (a) stick out some CNTs (labeled by G1) at the top of the array (figure 3(a)); (b) pull out CNTs G1 from the top to the bottom of the array (figure 3(b)); (c) CNTs G1 stick out adjacent CNTs (labeled by

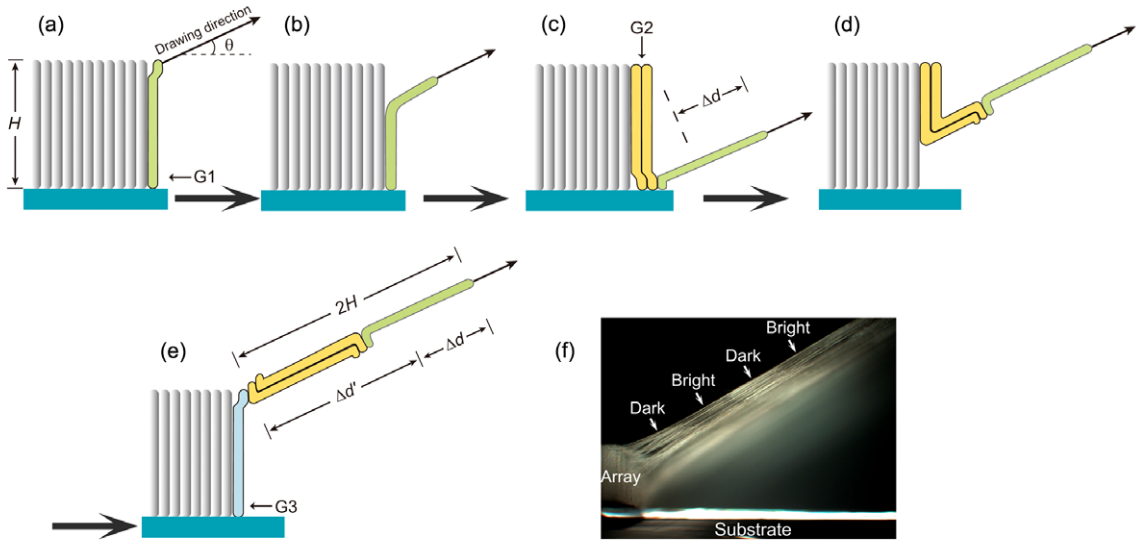

Figure 3. Drawing process at a drawing angle θ. (a)–(e) Five steps of the drawing process as described in the text. (f) Optical image of an as-drawn film connected with the top of a 410 μm high SACNT array. The image was taken in a dark-field mode, with a contrast inverse to the images in figures 1 and 2.

G2) at the bottom of the array (figure 3(c)); (d) pull out CNTs G2 from the bottom to the top of the array (figure 3(d)); (e) CNTs G2 stick out adjacent CNTs (labeled by G3) at the top of the array, and then a new cycle starts (figure 3(e)).

Here we should note that steps (a)–(c) and steps (c)–(e) are two subprocesses indicating that CNTs are pulled out from the SACNT arrays along two opposite directions. Next we will qualitatively analyze these two subprocesses and show the difference between them at a large drawing angle that contributes to the formation of stripes.

In the drawing process, while the SACNT film is drawn by a motor at a constant drawing speed, CNTs at the film–array interface are pulled out from the SACNT array continuously, forming new sections of the SACNT film. Therefore there is a relationship between drawing an SACNT film and pulling-out CNTs. We define that the drawing speed of the SACNT film is V_f, the pulling-out speeds of CNTs in steps (a)–(c) and steps (c)–(e) are V_c and V_c', respectively, the array height is H and the prime drawing angle is θ (figure 3(a)). After one cyclic drawing process, two bundles of CNTs are pulled out from the SACNT array and the drawing distance of the SACNT film is two times the array height, $2H$ (figure 3(e)). During the drawing process, the length of the drawn film is much larger than the array height H. Thus all of the drawing angles in each step (a)–(e) can be considered as the same value, θ. For the drawing process from step (a) to step (c), the drawing distance of the SACNT film can be calculated to be $\Delta d \approx H(1 - \sin\theta)$. Thus the duration in steps (a)–(c) is equal to about $H(1 - \sin\theta)/V_f$. The drawing distance of the SACNT film during steps (c)–(e) can be calculated to be $\Delta d' = 2H - \Delta d \approx H(1 + \sin\theta)$, and the duration in steps (c)–(e) is about $H(1 + \sin\theta)/V_f$. At a small drawing angle, $\sin\theta$ can be neglected, and the durations in steps (a)–(c) and steps (c)–(e) are equal, resulting in uniform SACNT films. However, at a large drawing angle, $\sin\theta$ cannot be neglected, and thus steps (a)–(c) are a faster subprocess compared to steps (c)–(e). As can be seen in movie S1 (available at stacks.iop.org/Nano/20/335705), the durations of steps (a)–(c) and steps (c)–(e) are about 1.0 s and 1.9 s, respectively. The different durations in these two subprocesses directly result in different pulling-out speeds of CNTs, i.e. $V_c > V_c'$, which may lead to different quantities of CNTs drawn out in these two subprocesses and further results in stripes in the films.

The stripes in the film possess an undulating character, which mainly originates from the start-up of drawing using the glass plate. When we used the glass plate to stick to the array, it was hard to hold the glass plate strictly parallel to the top surface of the array. As a result, some CNTs might stick to the glass plate with their top ends, some with their side walls and others with their bottom ends. Then when we pulled the glass plate, drawings of CNTs at different positions would be started at different steps of the cyclic drawing process. It means that, at the same time, CNTs at some positions may be drawn out forming a bright part, while CNTs at other positions may be drawn out forming a dark part. This inconsistency induces the undulating character of the stripes.

To determine which subprocess produces thick or thin sections of the film, we took a still image during the drawing process using an optical microscope in a dark-field mode. As shown in figure 3(f), a striped film is connected with the top of an SACNT array, indicating the drawing process at that time is in either step (a) or (e). It suggests that the thicker section of the film adjacent to the array was formed in steps (c)–(e), while the next adjacent thinner section was formed in steps (a)–(c). Therefore the sections of the film pulled out from the bottom to the top of the array (slower subprocess) are dark stripes (thicker section), while the sections pulled out along the inverse direction (faster subprocess) are bright stripes (thinner section).

In both steps (a)–(c) and steps (c)–(e), CNTs throughout the whole height of the SACNT array are pulled out to form stripes. Therefore the widths of the dark and bright stripes

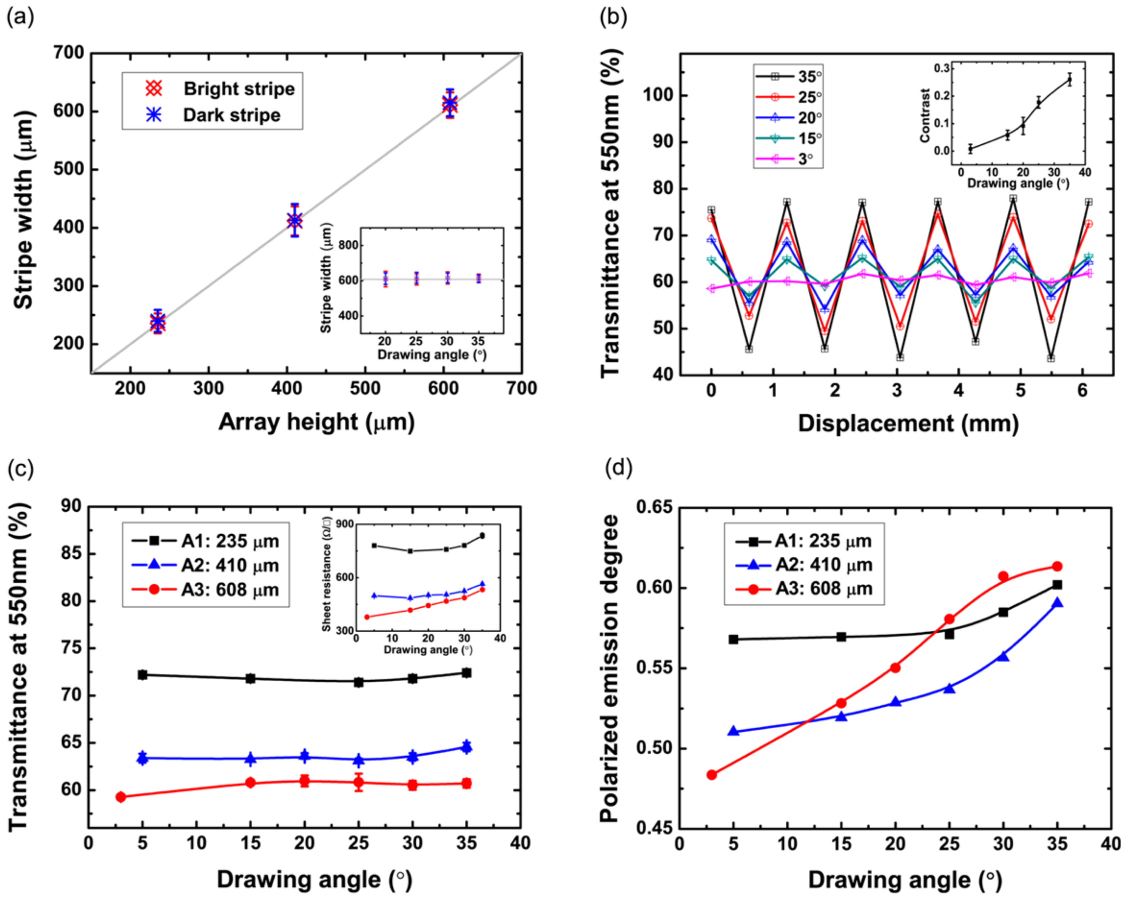

Figure 4. Properties of striped SACNT films. (a) Dependence of the width of stripes on array height at a drawing angle of 35°. The diagonal line marks positions where the width of the stripe equals the height of the SACNT array. The inset shows the relationship between the stripe widths and the drawing angles for films drawn from a 608 μm high SACNT array. (b) Transmittances of dark and bright stripes for films drawn from a 608 μm high SACNT array at various drawing angles. The inset shows the dependence of stripe contrast on the drawing angle. (c) Dependence of the mean film transmittance and the sheet resistance (inset) on drawing angle. (d) Dependence of the degree of polarized light emission on drawing angle. The legends of figures (c) and (d) indicate three groups of SACNT films: (1) A1: drawn from a 235 μm high SACNT array; (2) A2: drawn from a 410 μm high SACNT array and (3) A3: drawn from a 608 μm high SACNT array.

should be equal to the height of the SACNT array, which is further proved by the statistical data in figure 4(a). Moreover, the stripe widths do not depend on drawing angles (inset of figure 4(a)). However, with increasing drawing angle, steps (a)–(c) and steps (c)–(e) diverge more and more clearly, and the transmittances of the bright and dark stripes vary accordingly (figure 4(b)). Here we define the stripe contrast as $(\overline{T_b} - \overline{T_d})/(\overline{T_b} + \overline{T_d})$, where $\overline{T_b}$ and $\overline{T_d}$ are mean transmittances of bright and dark stripes, respectively. As shown in the inset of figure 4(b), the stripe contrast increases with increasing drawing angle, from about 0 at 3° to 0.26 at 35°. It indicates that, when the drawing angle is small, the SACNT film tends to be uniform; but with increasing drawing angle, the film becomes striped more and more clearly. Although the stripe contrasts are different at various drawing angles, the mean film transmittance does not depend on drawing angles obviously (figure 4(c)). Since the transmittance depends on the quantity of CNTs in the film, this phenomenon suggests that nearly the same quantity of CNTs is pulled out from an SACNT array whether at large drawing angles or small ones. However, the sheet resistance shows slight variation at different drawing angles (inset of figure 4(c)), which is caused by different CNT distributions or different contact resistances of CNT junctions due to the change of the film configuration.

The drawing process described above also indicates that the boundaries between dark and bright stripes should be composed of CNT junctions, which is consistent with the result shown in figure 2(d). The convenient observation of such CNT junctions provides a way to study their effects on film properties, e.g. thermal, electrical and mechanical properties.

To study their effects on electrical and thermal properties of the film, a dc current was applied to a striped SACNT film in vacuum. For a 1.0 cm (L) × 1.5 cm (W) striped film drawn from the 608 μm thick array, the dc current that induces visible light is in the range of 0.15–0.30 A, while upon 0.30 A, the striped film will break down. The bright stripes in the film emitted much stronger visible light than dark stripes did, inducing striped emitting light (figure 5(a)). The striped emission suggests that most of the heat induced by the dc current is produced in the bright and thin stripes because of their smaller cross-sectional area and thus high resistance, and further restricted in the bright stripes by the CNT junctions. Thus the

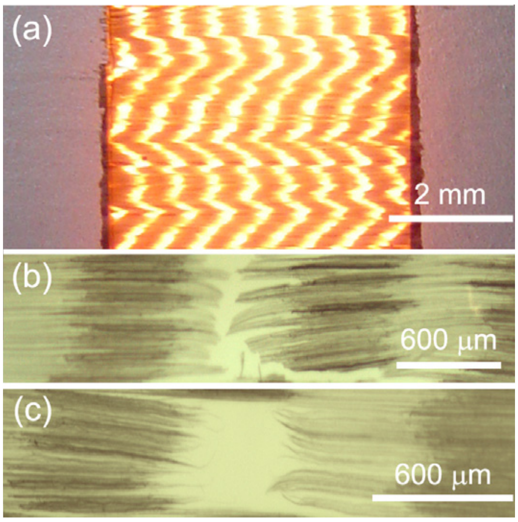

Figure 5. Characterization of striped SACNT films. (a) A striped SACNT film between two silver electrodes under a dc current in vacuum. (b) Breakdown position by a large dc current in vacuum. (c) Breakdown position by a pulling process. The films in these three figures were all drawn from a 608 μm high SACNT array.

CNT junctions are bottleneck positions for thermal conduction. Nevertheless, as shown in movie S2 in the multimedia file (available at stacks.iop.org/Nano/20/335705), with increasing dc current, the position initially emitting visible light is located around the midst of the bright stripes, rather than at the CNT junction. Moreover, the breakdown points induced by a large dc current are also around the same position (figure 5(b)). Therefore it is the midst of the bright stripes that possesses the highest temperature under a dc current, which indicates that the CNT junctions are not high-resistive positions and should not limit the electrical conduction of the film.

To study the effect of CNT junctions on the mechanical properties of the film, we fixed a freestanding striped SACNT film on two separate cantilevers, and moved the cantilevers apart along the drawing direction to pull and break the film. As shown in figure 5(c), the breakdown position is located at the boundary between the bright and dark stripes, indicating that the CNT junctions are weakly joined and therefore being bottleneck positions for the mechanical strength of the film.

Among optical applications of SACNT films, a promising one is as a planar polarized light source [10, 11], which is attributed to the unidirectional alignment of CNTs in the SACNT films. Generally, light emission from a thick SACNT film, e.g. a film drawn from an SACNT array with a height greater than 500 μm, has a small polarization degree (usually <0.5), while light emission from a thin film has a large polarization degree [11]. However, a striped SACNT film, produced from either a high or a low SACNT array, has a highly polarized emission, since the sections of the film with strong emission are the bright stripes with small thickness and large polarization degree. Figure 4(d) shows the relationship between the drawing angle and the polarization degree for films drawn from SACNT arrays with different heights. At a small drawing angle, the polarization degree negatively depends on the height of the SACNT array, in accordance with our former result [11]. The increase of the drawing angle enhances the polarization degree of the films drawn from SACNT arrays with different heights. For a higher SACNT array, the polarization degree increases faster. At a drawing angle of 35°, the polarization degrees of all three samples increase to about 0.6. This value is much larger than those at small drawing angles, especially for the thick and robust films produced from the 410 and 608 μm high SACNT arrays, which show a great improvement in polarized emission. Therefore drawing films with a large drawing angle provides a convenient way to tune the polarization degree, and further produce a high-degree polarized and striped emitting light source.

Furthermore, by controlling the height of the SACNT array, we can tune the periodic width of stripes in SACNT films, which may be used as optical coherent devices of certain wavelengths. Because of the striped configuration, the striped films may be used as a template to prepare other striped structures. In addition, the CNT junctions located at the boundary of the stripes are usually defective due to the CVD process, and thus chemically reactive. Therefore the striped films provide a special substrate to study some chemical reactions or biological processes. This will be favorable for improving the properties of the films and may open up some new applications such as biomaterials in the future.

4. Summary

To summarize, we produced striped SACNT films from SACNT arrays at large drawing angles. The width of the periodic stripes in the films equals the height of the SACNT arrays, resulting from the difference in the two subprocesses during the drawing process. Our result validated the model of end-to-end joining of CNTs for forming SACNT films. The CNT junctions in the striped films can be easily observed and identified at the boundary of the stripes. We further studied the effects of these CNT junctions on the mechanical, thermal and electrical properties of the films, and found that the striped film can be utilized as a high-degree polarized and striped emitting light source. Our new method deepens the basic understanding of the drawing process of SACNT films from SACNT arrays, and will be valuable for new applications and future large-scale production of tunable SACNT films.

Acknowledgments

This work was financially supported by the National Basic Research Program of China (2005CB623606 and 2007CB935301), NSFC (10704044, 50825201 and 10721404), the Fok Ying Tung Education Foundation (111049) and the China Postdoctoral Science Foundation (20080440025). We thank Professor Yadong Li and Qiuqiu Zheng for their help in this work.

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