A general surface-treatment-free approach to fabrication of alignment layers using a super-aligned carbon nanotube film template*

Fu Wei-Qi(付伟琦), Wei Yang(魏 洋), Zhu Feng(朱 峰), Liu Liang(刘 亮)†
Jiang Kai-Li(姜开利), Li Qun-Qing(李群庆), and Fan Shou-Shan(范守善)

Department of Physics and Tsinghua–Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, *China*

(Received 22 February 2010; revised manuscript received 3 March 2010)

We develop a general approach to the fabrication of films with unidirectional grooves, such as silicon nitride, silicon dioxide and aluminium oxide, in which the surface is not required to be treated. Super-aligned carbon nanotube (SACNT) film may be used as a template and as sacrificial layer, which is subsequently removed by heating in an atmosphere of air. The unidirectional morphology of the SACNT film turns into a desired film, which is found to possess the ability to align liquid crystal molecules. This approach also features high efficiency, low cost and easy scaling-up for mass production.

Keywords: super-aligned carbon nanotube film, alignment layer, template

PACC: 8120, 8115H

1. Introduction

Carbon nanotubes (CNTs) have attracted a great deal of attention since their discovery by Iijima[1] because of their widespread potential applications. Recently, a new type of CNT, known as super-aligned carbon nanotube (SACNT) film, has been fabricated by our group,[2−4] and a number of novel applications have been found based on it, such as thin film loudspeaker,[5] micro-grids for high resolution transmission electron microscopy (HRTEM) for nanomaterials,[6] incandescent displays,[7] and high-capacity anode materials for lithium-ion batteries.[8] Baughman *et al.*[9−12] have also fabricated similar materials and developed some applications. However, the most important property of SACNT film, the unidirectional nature, has not yet been fully explored. In the present paper, we develop an application based on the unidirectional property of this film.

As is well known, aligning liquid crystal (LC) molecules into a stable and uniform layer over a large area is vital for the fabrication of high-quality liquid crystal display (LCD). Of many methods, the preferred modification technique used in mass production is mechanical rubbing. Extending the traditional rubbing process which treats the polyimide with a cloth-covered roller, Varghese *et al.*[13] used a macroscopic metallic object. This opened new possibilities for the micro-patterning of alignment layers. However, this method could not be applied to hard inorganic films and was not efficient. Chaudhari *et al.*[14] used low-energy ion-beams impinging on the diamond-like carbon film to form an alignment layer. In our method, alignment layers are formed by using the SACNT film as a template and sacrificial layer. Different materials such as silicon dioxide, silicon nitride, and aluminium oxide can be modified in this way, without surface treatment prior to use and with high efficiency and low cost. In the present paper described are the use of silicon nitride as an example to illustrate the method and its application to aligning liquid crystal molecules.

2. Experiment

Figure 1 illustrates the fabrication process. Figure 1(a) shows a glass substrate with a thickness of 1.2 mm. A layer of SACNT film was then drawn from

*Project supported by the National Basic Research Program of China (Grant Nos. 2005CB623606 and 2007CB935301) and the National Natural Science Foundation of China (Gant Nos. 10704044, 50825201, and 10721404).
†Corresponding author. E-mail: liuliang@tsinghua.edu.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

a super-aligned CNT array and then attached to the surface of the substrate. After wetting by ethanol and drying in air, the CNT film adhered tightly to the substrate by the van der Waals interaction as shown in Fig. 1(b). A target layer of silicon nitride, with a thickness of 50 nm, was deposited on the SACNT film by plasma enhanced chemical vapour deposition (PECVD) as shown in Fig. 1(c). Finally, the SACNT film was removed by thermal treatment in a muffle furnace. We raised the temperature from room temperature to 522 °C in 2 h, maintained it for 0.5 h, and then allowed the SACNT film to naturally cool down to room temperature. A silicon nitride film with uni-directional grooves was thus fabricated by using the SACNT film as a template. The morphology is shown in Fig. 1(d).

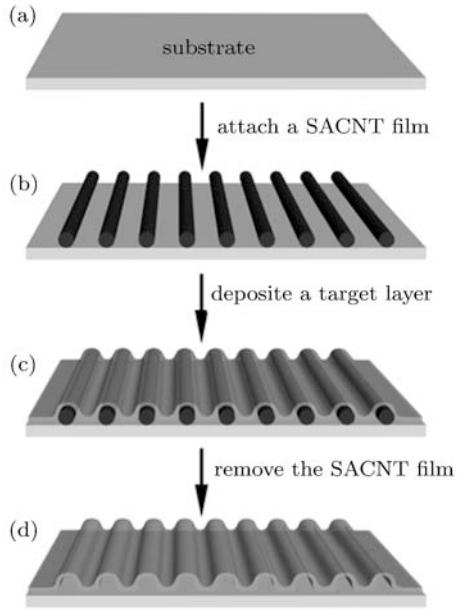


Fig. 1. A schematic illustration of the fabrication processes. (a) A clean glass substrate, (b) a SACNT film-coated substrate, (c) the target layer grown on the CNT-coated glass by the PECVD method, and (d) the CNT removed by thermal treatment in air giving an alignment layer composed of the target material.

3. Results and discussion

Figure 2 shows scanning electron microscopy (SEM) images of the aligned silicon nitride film. From the low magnification image, Fig. 2(a), we can see that the film has good uni-directionality. Figure 2 (b) shows that the width of the aligned unit (the quasi-silicon nitride tube) is about 100 nm, much larger than the diameter of the CNT in the SACNT film, which is about 10–15 nm. This scale corresponds more closely to the thickness of the film, 50 nm. The morphologies of the silicon nitride film demonstrate that our approach, even without surface treatment prior to use, does not destroy the aligned structure, preserving the morphology very well. We conclude that such an approach is effective and reliable.

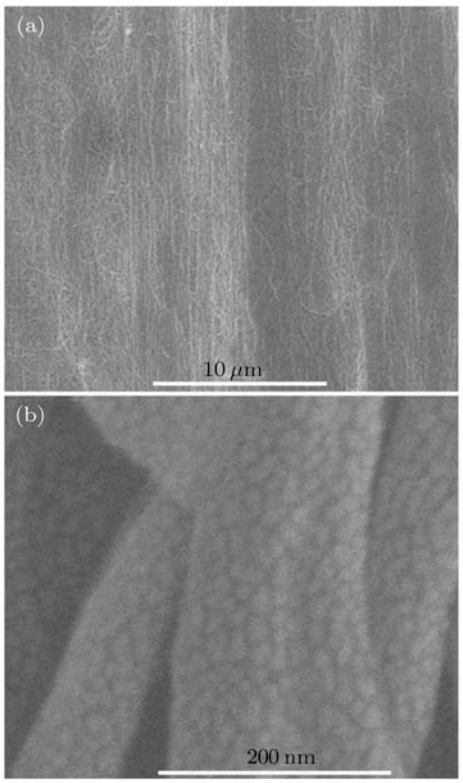


Fig. 2. SEM images of aligned silicon nitride film at low (a) and high (b) magnifications.

The Raman spectroscopy studies, shown in Fig. 3(a), can prove that the SACNT film has been successfully removed by thermal treatment. Before the thermal treatment, we observed two characteristic peaks: the D-band (∼1353 cm^{-1}) and the G-band (∼1587 cm^{-1}). After the treatment, these two peaks disappeared, meaning that the SACNT film had been removed. Figure 3(b) also indicates that the SACNT film is removed. The light transmission of the substrate after treatment is 95.02%, which is close to that of the plain substrate, 98.21%, and significantly higher than that of substrate with SACNT film, which is 76.89%. From the conductance aspect, we find that the square resistance of the substrate after treatment is more than 200 MΩ/□, which is larger than that of substrate before treatment, 1.2 kΩ/□. So we can conclude that the SACNT film can be entirely removed away in this treatment process. The morphology shown in Fig. 2 is just from the silicon nitride film and with no influence from the SACNF film.

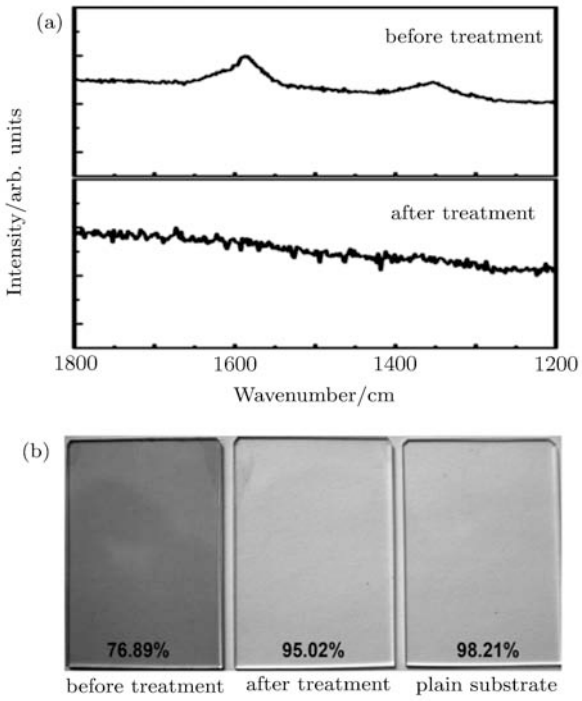


Fig. 3. (a) Raman spectra of the sample before and after thermal treatment, and (b) light transmissions of the substrate before and after treatment compared with that of the plain substrate.

In our previous work,[15] we fabricated a liquid crystal display (LCD) cell with SACNT film serving as an alignment layer. We found that the SACNT film worked well. From the fabrication process mentioned above and the SEM images, we know that the aligned silicon nitride film matches the morphology of the SACNT film. Accordingly, we can expect that such a film has the same alignment effects but with much higher transparency and without increasing the conductivity. To test the alignment effect of such an aligned film, we sandwiched an appropriate quantity of liquid crystal (LC) between two glass panels coated by such films, placed in such a way that they are opposite and perpendicular to each other. In order to obtain a uniform spacing between the two panels, we used polyethylene spheres, 5 μm in diameter, as spacers.

We used polarized light incident on the back of the LCD cell, with its polarization direction perpendicular to the film surface, and a second polarizer in front of the cell, whose polarization direction was perpendicular to the first one. Figure 4 shows the optical image of the LCD cell. The white image means the polarized incident light can pass through the second polarizer with the help of the twisted LC molecules, whose alignment direction was determined by the aligned silicon nitride film. The result gives us the evidence that the as-prepared film can preserve its alignment property.

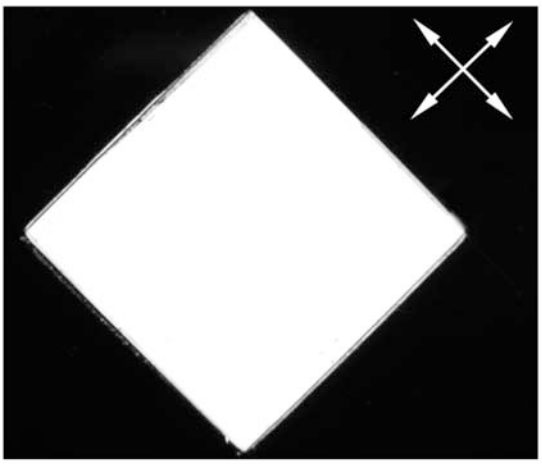


Fig. 4. Optical image of LCD cell with an aligned silicon nitride film used as alignment layer. The crossed white arrows show the polarization directions.

Our technique described above, without requiring surface treatment, is a rather general method of fabricating various films. Figure 5 shows SEM images of (a) silicon dioxide film and (b) aluminium oxide film prepared by using the same approach. The as-prepared films also well retain the ability to align LC molecules as shown in Figs. 5(c) and 5(d).

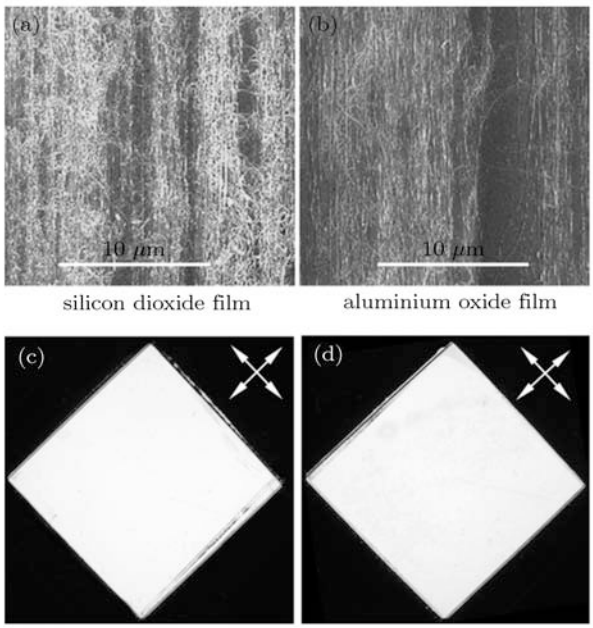


Fig. 5. SEM images of (a) silicon dioxide film and (b) aluminium oxide film prepared by using the same technique, without any surface treatment; (c) and (d) are the images corresponding to (a) and (b), which show the alignment effect. The crossed white arrows show the polarization directions.

4. Conclusion

We developed a general method to fabricate various films with unidirectional grooves. SACNT film is used as a template and sacrificial layer, subsequently removed by heating in an atmosphere of air. The morphology of the SACNT film turns into a desired film. By removing the SACNT film, the light transmission of the substrate is improved to that of the plain substrate. Various films prepared in this way can be used as suitable alignment layers for the manufacture of LCDs. The films are hard, transparent and insulating, and they have ideal properties for serving as alignment layers. This technique, with no surface treatment required, is general and is not limited to any special material. It requires only that the film itself is not destroyed in the thermal treatment process. This technique also features high efficiency, low cost and easy scaling-up for mass production.

Acknowledgment

We thank Xiao Lin, Liu Kai and Liu Peng for reading of the paper and also Xu Li-Guo and Yin Chang-Qing for helping grow target films.

References

[1] Iijima S 1991 *Nature* **354** 56
[2] Jiang K L, Li Q Q and Fan S S 2002 *Nature* **419** 801
[3] Zhang X B, Jiang K L, Teng C, Liu P, Zhang L, Kong J, Zhang T H, Li Q Q and Fan S S 2006 *Adv. Mater.* **18** 1505
[4] Liu K, Sun Y H, Chen L, Feng C, Feng X F, Jiang K L, Zhao Y G and Fan S S 2008 *Nano Lett.* **8** 700
[5] Xiao L, Chen Z, Feng C, Liu L, Bai Z Q, Wang Y, Qian L, Zhang Y Y, Li Q Q, Jiang K L and Fan S S 2008 *Nano Lett.* **8** 4539
[6] Zhang L, Feng C, Chen Z, Liu L, Jiang K L, Li Q Q and Fan S S 2008 *Nano Lett.* **8** 2564
[7] Liu P, Liu L, Wei Y, Liu K, Chen Z, Jiang K L, Li Q Q and Fan S S 2009 *Adv. Mater.* **21** 3563
[8] Zhang H X, Feng C, Zhai Y C, Jiang K L, Li Q Q and Fan S S 2009 *Adv. Mater.* **21** 2299
[9] Zhang M, Fang S L, Zakhidov A A, Lee S B, Aliev A E, Williams C D, Atkinson K R and Baughman R H 2005 *Science* **309** 1215
[10] Williams C D, Robles R O, Zhang M, Li S, Baughman R H and Zakhidov A A 2008 *Appl. Phys. Lett.* **93**
[11] Kuznetzov A A, Lee S B, Zhang M, Baughman R H and Zakhidov A A 2010 *Carbon* **48** 41
[12] Ulbricht R, Lee S B, Jiang X M, Inoue K, Zhang M, Fang S L, Baughman R H and Zakhidov A A 2007 *Sol. Energy Mater. Sol. Cells* **91** 416
[13] Varghese S, Narayanankutty S, Bastiaansen C W M, Crawford G P and Broer D J 2004 *Adv. Mater.* **16** 1600
[14] Chaudhari P, Lacey J, Doyle J, Galligan E, Lien S C A, Callegari A, Hougham G, Lang N D, Andry P S, John R, Yang K H, Lu M H, Cai C, Speidell J, Purushothaman S, Ritsko J, Samant M, Stohr J, Nakagawa Y, Katoh Y, Saitoh Y, Sakai K, Satoh H, Odahara S, Nakano H, Nakagaki J and Shiota Y 2001 *Nature* **411** 56
[15] Fu W Q, Liu L, Jiang K L, Li Q Q and Fan S S 2010 *Carbon* **48** 1876